NASA-CR-72464
MRB5014F

Final Report
RESEARCH AND DEVELOPMENT OF THE DRY TAPE BATTERY CONCEPT
1 July 1967 - 30 June 1968

Contract No. NAS3-9431

1 September 1968

For

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LIST OF ABBREVIATIONS

DCA-70	Dichloroisocyanuric acid. Monsanto Co. ACL-70® was used in this study.
TCA-85	Trichloroisocyanuric acid. Monsanto Co. ACL-85® was used in this study.
MF	Methyl formate
4A MF	Methyl formate Chromatographed over Linde 4A molecular sieves
SAB	Shawinigan acetylene black
CF	Carbon fibers
ACL No.	Active chlorine number. Determined by iodide-thiosulfate titration. A measure of the capacity relative to Cl_2 = 100.
WB	Waring blender
BM	Ball mill blender
PK	Patterson-Kelly blender

SUMMARY

Work in this laboratory under contract NAS3-7624 showed that the Li/$LiClO_4$-methyl formate/DCA-70* system would produce energy densities in excess of 200 watt-hr/lb, based on anode, cathode, separator, and electrolyte weights. The program was designed to increase the cathode efficiency and current density of this cell while retaining the high energy density previously demonstrated. The high current densities are necessary for advantageous use of the Dry Tape concept.

The highlights of the present investigation are summarized below:

1. The electrolyte solvent used on Contract NAS3-7624 was found to contain 4% methanol. This was removed by passing the solvent through a column of Linde 4A molecular sieves. Removal of this methanol decreased DCA-70 decomposition and lithium gassing in the electrolyte solvent. In full cell tests, however, these improvements led to only marginal changes in cell performance.

2. The commercial DCA-70 material was found to contain 10% sodium salt of dichloroisocyanuric acid. This salt has a lower solubility in the solvent and also poorer discharge characteristics than DCA-70. Purification of DCA-70 by recrystallization in methyl formate did not improve cell performance.

3. DCA-70 decomposition is accelerated by chloride ions. However, under Dry Tape discharge conditions the decomposition by LiCl would not lead to a serious efficiency loss.

4. $LiAsF_6$ provides a higher conductivity in methyl formate than $LiClO_4$ (ref. 4). Although an average voltage improvement is observed in our system, no improvement in rate or efficiency was possible by the use of this electrolyte. DCA-70 solubility and gassing at 4°C is decreased by the use of this electrolyte.

5. The increase of $LiClO_4$ concentration above 2 molar does not increase the maximum rate of cell discharge. An increase was anticipated based on Li/CuF_2 performances (ref. 8).

*DCA-70 = Dichloroisocyanuric Acid (ACL-70®).

6. Chronopotentiometry of DCA-70 at smooth platinum showed that the electroreduction is irreversible ($\alpha n_a = 0.07$). However, no separate voltage steps are involved. Four electrons are transferred per molecule and the diffusion coefficient of DCA-70 in the electrolyte is 1.4×10^{-6} cm^2/sec. Chronopotentiometry with current reversal indicates a soluble product which can be re-oxidized. This product could be chloride ion.

7. Coulometry of DCA-70 produced an insoluble organic product which passivated the electrode surface. This product has an infrared spectrum similar to a literature spectrum of cyanuric acid.

8. Cell gassing was observed when a gas-tight cell was developed in a company-sponsored program. This gassing is approximately 15cc(STP)/A-hr, under ambient-temperature, 3-hour rate discharge conditions. This gas is approximately 50% methyl formate vapor. Using 2M $LiAsF_6$ and testing at 4°C only 3 cc(STP)/A-hr is obtained.

9. A correlation was obtained between cell discharge efficiency and conductivity of cathode blends as blended by various methods. An inverse correlation was obtained between time of blending and cell performance. Overblending is detrimental, especially when blends were obtained by ball milling. By pre-fluffing the carbon black and pre-grinding the DCA-70, Waring blend times of 5 seconds and twin-shell blend times of 10 minutes could be used. However, obvious visual heterogeneities are present in such blends.

10. Highest efficiencies and rates were obtained with thin cathodes. High carbon content or high void volume also improved efficiency and high rate performance. In these areas a trade-off is required between the rate and efficiency increase and energy density decrease. The discharge data below summarize the capabilities of the present system.

CONSTANT VOLTAGE DATA (3.2 VOLTS)

Loading ($A\text{-}min/cm^2$)	Cathode Efficiency (%)			Energy Density[1] (w-hr/lb)		
	30 min	60 min	480 min	30 min	60 min	480 min
23	23	35	69	68	102	203
14	34	52	75	74	112	163

[1] Energy density based on weights of anode, cathode, separator and electrolyte. Anode weight is unnecessarily high and adversely effects very high rate data.

CONSTANT CURRENT DATA

Loading (A-min/cm^2)	Current Density (mA/cm^2)	Cathode Efficiency (%)	Energy[1] Density (w-hr/lb)	Discharge Time to 2.0 volts (min)
23[2]	10	63	146	148
21[3]	10	58	158	122
8	15	64	89	33
3	25	54	69	6

[1] Energy density based on weights of anode, cathode, separator and electrolyte. Anode weight is unnecessarily high and adversely effects very high rate data.

[2] 17% carbon in cathode

[3] 25% carbon in cathode

11. The Li/DCA-70 system can be stored in an Aclar 33C envelope. Heat sealed packets were discharged after 3 months without noticeable performance loss. The envelope weight penalty is 18 mg/cm^2, or 9% based on the standard tape (23 A-min/cm^2 activated tape).

I. INTRODUCTION

A. THE DRY TAPE CONCEPT

A Dry Tape battery consists of (1) a thin separator tape sandwiched between a dry anode and a dry cathode coating, and (2) an electrolyte supply. The tape is fed continuously or intermittently between a set of current collectors. The electrolyte is added just before the tape cell passes between the collector plates. This allows the undischarged tape to remain dry and provides the electrochemical cell with stop-start reserve capability and allows the use of high energy reserve type components.

In addition to having extended shelf life, a Dry Tape device can be designed to minimize some of the common limitations of conventional batteries; such as reactant depletion, reaction product build-up and separator deterioration. Because of the continuous supply of fresh reactants and the removal of reaction products from the current collector area, a constant potential and power output is maintained. By using a compact electrode spacing with minimum separator thickness, the dry tape can be designed for high-rate discharges of the small activated section.

B. DRY TAPE BACKGROUND

The work described in this report is a continuation of research performed under Contracts NAS3-2777, NAS3-4168 and NAS3-7624.

During the initial program (NAS3-2777), the feasibility of the Dry Tape concept was demonstrated using a divalent silver oxide-coated, porous polypropylene tape that was drawn between two current collectors. One current collector was a zinc block that also served as the anode. The cathode current collector was a thin silver plate. Electrolyte was supplied by a second tape, prewet with electrolyte, and stored separately ("dual tape system").

In a follow-on program (NAS3-4168), the "dual tape system" was replaced by a single tape configuration using a thin foil magnesium anode and cathode coatings containing high energy organic and inorganic depolarizers. Efficient, high drain rate discharge of these cathode materials was achieved through use of the "thin-plate tape electrode" configuration. The single-tape configuration was optimized for the system, Mg/2M $AlCl_3$; 0.5M HCl/KIO_4. Up to 80% KIO_4 utilization was achieved with a cell voltage of 2.2 volts at a current density of 0.5 amp/in.^{2} while in a moving configuration. Energy densities approaching

80 watt-hr/lb were obtained. In addition to electrode configuration development, methods of electrolyte encapsulation and tape activation were devised. Also, techniques for supplying multiple cell voltage, parasitic drive, and continuous coated tape manufacture were developed.

Emphasis was placed on the development of a high energy density electrochemical couple during the next contract period (NAS3-7624). The $Li/LiClO_4$(MF)/DCA-70 cell was demonstrated to give, reproducibly, energy densities in excess of 200 watt-hr/lb based on the weights of anode, cathode, separator and electrolyte. The Mg/aq. $MgBr_2$/TCA-85 gave 120 watt-hr/lb and was demonstrated in a dynamic Dry Tape configuration.

C. CONTRACT OBJECTIVE

Performance data indicated that the cathode was the limiting factor in the Li/DCA-70 cell. Tests which gave 200 watt-hr/lb showed cathode efficiencies of only 65 to 70 percent. The objective of the present work (NAS3-9431) therefore, was the optimization of the DCA-70 cathode.

High current density, consistent with high energy density, adequate tape strength, and tape protection were the specific objectives of this contract.

II. RESULTS AND DISCUSSION

A. ELECTROLYTE PROPERTIES

1. $LiClO_4$-Methyl Formate Electrolyte

a. Introduction

Data obtained during previous work (ref. 1) indicated that the optimum $LiClO_4$-MF electrolyte concentration for the discharge of our Li/DCA-70 cell was 2 molar. The reason for this was unclear, since DCA-70 solubility was neither at a maximum nor a minimum, and the conductivity of the electrolyte was not maximum at this concentration. It was felt that electrolyte viscosity might correlate with maximum energy density. Therefore, (1) the kinematic viscosities of $LiClO_4$-MF solutions were determined as a function of electrolyte molarity, and (2) the viscosities of 2M $LiClO_4$-MF solutions were determined as a function of added DCA-70. In addition, studies of $LiClO_4$-MF electrolyte conductivity as a function of molarity were completed.

b. The Conductivity of $LiClO_4$-MF Solutions as a Function of Molarity

Complete conductivity data are shown in Figure 1. It should be noted that conductivity is maximum in 3 molar solutions, and decreases at 4 molar concentrations.

The conductivity was not influenced by MF purification. Solutions (2M) of $LiClO_4$ in standard and purified (4A molecular sieve treatment) methyl formate had identical conductivities (2.25×10^{-2} ohm^{-1} cm^{-1}).

c. The Viscosity of $LiClO_4$-MF Solutions as a Function of Molarity

Kinematic viscosities were determined with a Cannon-Fenske viscometer with a tube constant of 3.643×10^{-3} at 22°C. The viscosities reported in Tables 1 and 2 are the average of two determinations.

The data indicate that a large viscosity change occurs between 2 and 3 molar $LiClO_4$ (Figure 2). This may explain the energy density maximum in 2 molar solutions.

The viscosity of DCA-70 solutions indicates DCA-70 saturation at approximately 9 percent DCA-70 (Figure 3). This saturation value is slightly lower than that obtained from active chlorine titration data.

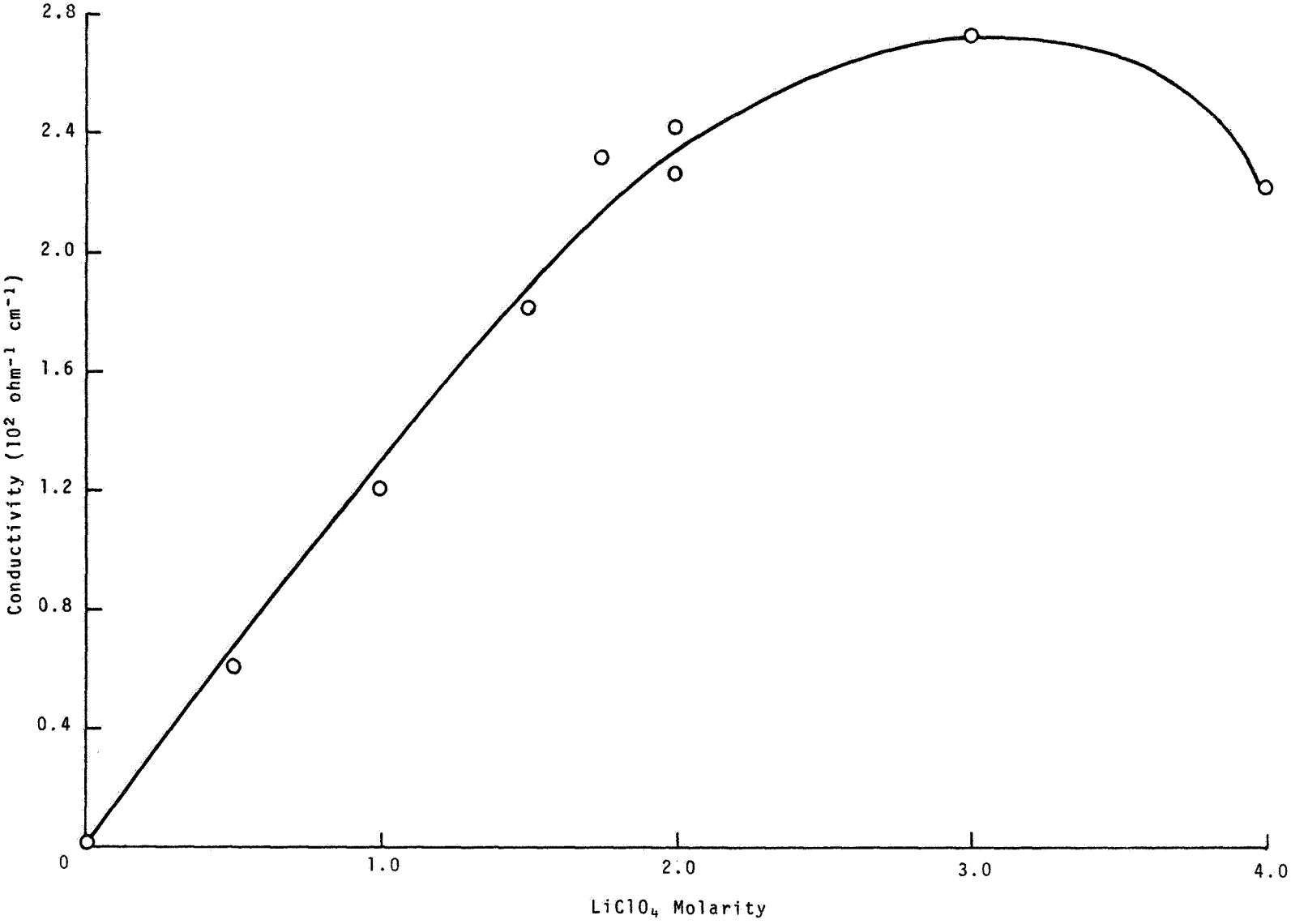


Figure 1. Conductivity of $LiClO_4$-Methyl Formate Solutions

Table 1

KINEMATIC VISCOSITIES OF $LiClO_4$-METHYL FORMATE SOLUTIONS

Concentration $LiClO_4$ (moles/liter)	Viscosity (centistokes)
0.0*	0.351
0.5	0.451
1.0	0.573
1.5	0.758
1.75	0.872
2.0	1.031
3.0	1.955
4.0	3.761

* Pure MF

Table 2

KINEMATIC VISCOSITIES OF 2M $LiClO_4$-MF SOLUTIONS CONTAINING DCA-70

Concentration DCA-70 (weight-%)	Viscosity (centistokes)
0.0	1.031
4.0	1.151
8.0	1.377
16.0	1.486

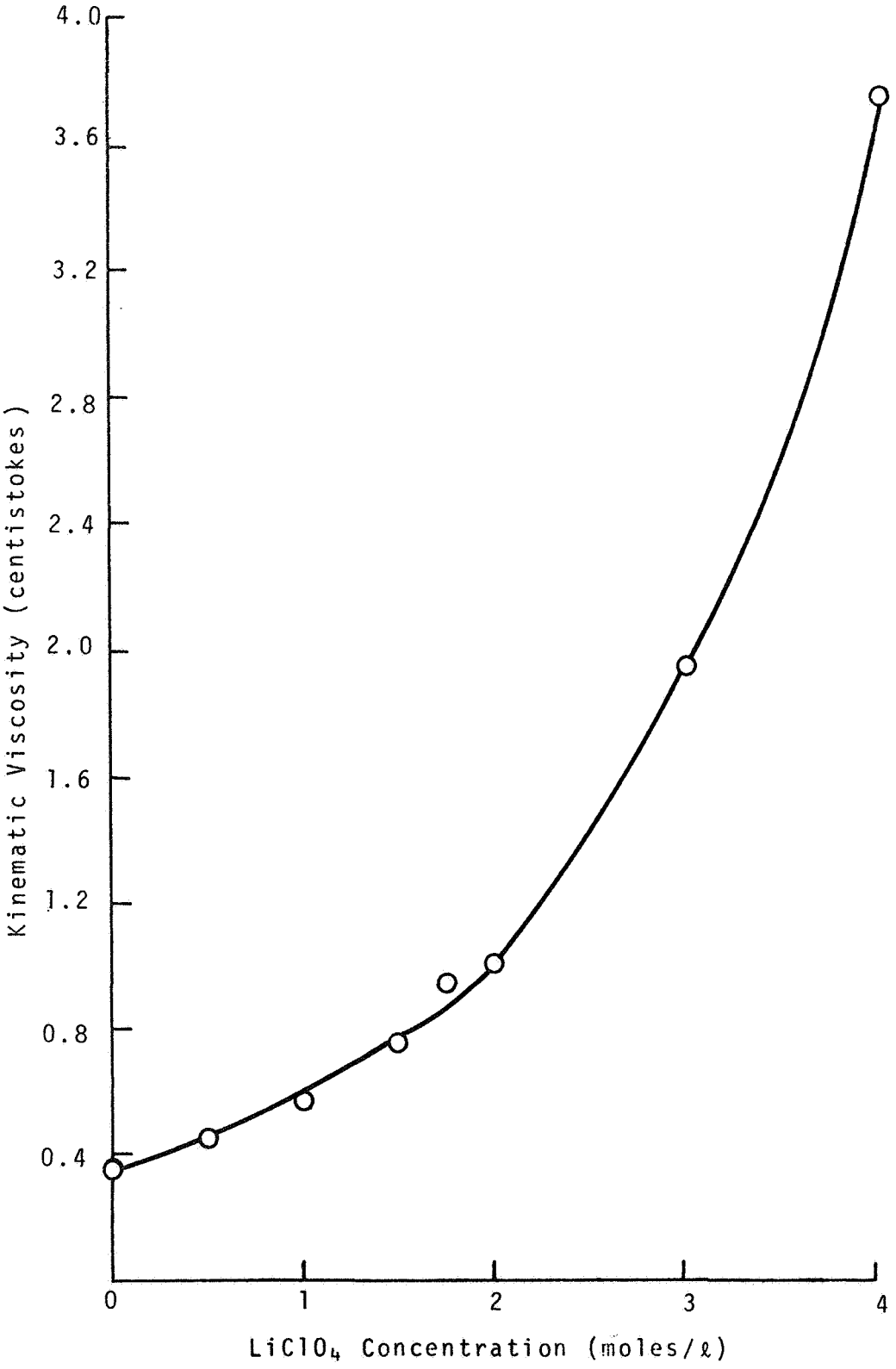


Figure 2. Viscosity of $LiClO_4$-Methyl Formate Solutions at 23.6°C

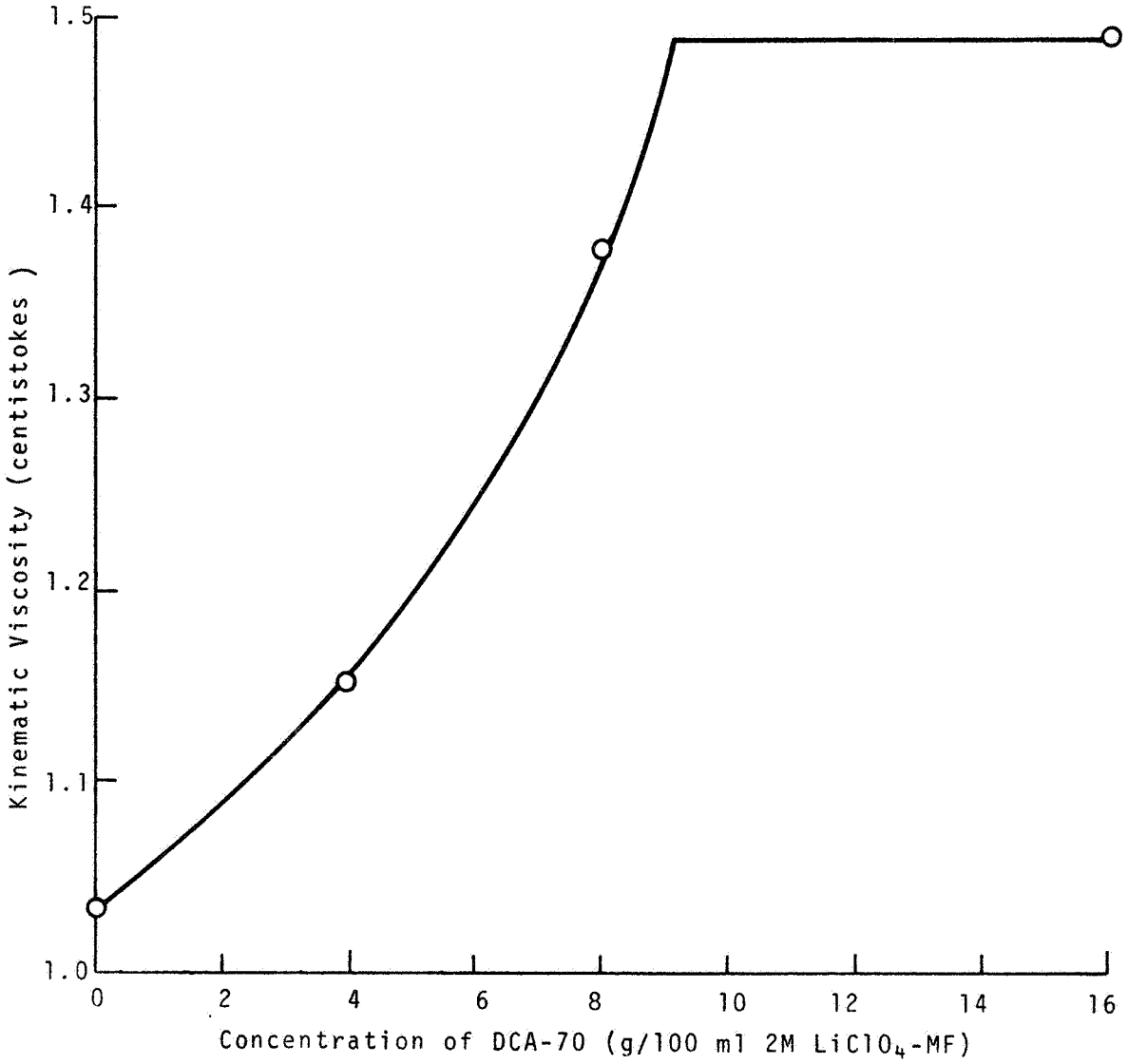


Figure 3. Viscosity of Solutions of DCA-70 in 2M $LiClO_4$-Methyl Formate

d. Conductivity-Viscosity Relationship for $LiClO_4$-MF Electrolytes

It is probable that high electrolyte conductivity and low electrolyte viscosity enhance battery discharge characteristics. If equal importance is assigned to both variables, then the larger the conductivity to viscosity ratio, the better the discharge characteristics should be. A plot of this ratio vs. molarity (Figure 4) indicates that the highest energy densities should be obtained using electrolyte in the 1.5 to 2.0 molar range. This is observed experimentally.

e. Properties of 2M $LiClO_4$-MF Electrolyte

(1) Conductivity of 2M $LiClO_4$-MF as a Function of DCA-70 Concentration

DCA-70 is soluble to the extent of 14% in 2M $LiClO_4$-MF electrolyte. The dissolved depolarizer changes the viscosity properties of the electrolyte (see above), with an increase from 1.0 to 1.5 centistokes. For this reason, the conductivity of the electrolyte as a function of DCA-70 concentration was obtained. This made possible better calculations on discharging cathodes. The data are presented in Figure 5, and show a decrease from 2.4×10^{-2} to 1.7×10^{-2} ohm^{-1} cm^{-1} due to the addition of DCA-70.

The conductivity of a solution of 8g DCA-70/100 ml MF was also measured. The value, 1×10^{-5} ohm^{-1} cm^{-1}, indicates that the hydroxylic hydrogen is not acidic in the sense of a free proton migration in the solvent.

(2) Solubility of LiCl in 2M $LiClO_4$(MF)

LiCl is one of the products of the Li/DCA-70 cell reaction. The solubility is known to be comparatively low. It is an unknown in our system which can be easily determined. An increase in solubility could improve the conductivity of electrolyte and also prevent precipitation as a thin film over the carbon reaction sites. Finally, Li^+ is generated at the anode, and if it is precipitated quantitatively at the cathode, then only Li^+ must carry current to maintain a constant electrolyte concentration throughout the cell. Since the transference number of Li^+ in $LiClO_4$(MF) is not 1.0, the cathode could lose $LiClO_4$ as in the Hittorf method for measuring transference numbers. This might be the reason for high $LiClO_4$ molarity improvement in Li/CuF_2 cells, and the reason for the constancy of $i\tau^{1/2}/C$, at high currents, where C is concentration of $LiClO_4$ (see Section IIC). The transference number for Li^+ would be expected to be 0.3-0.4 (refs. 2, 3).

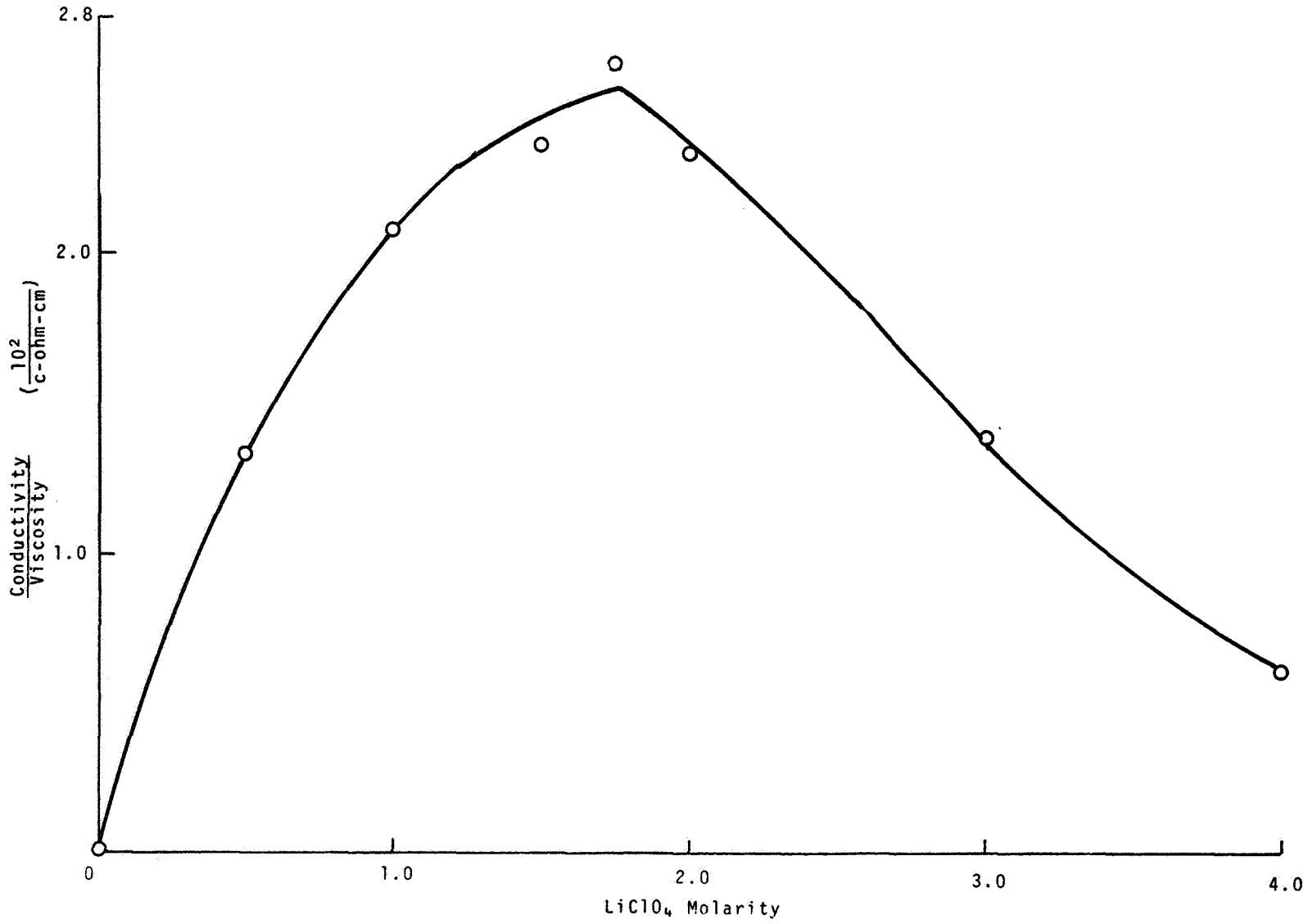


Figure 4. Conductivity-Viscosity Ratios for $LiClO_4$-Methyl Formate Solutions

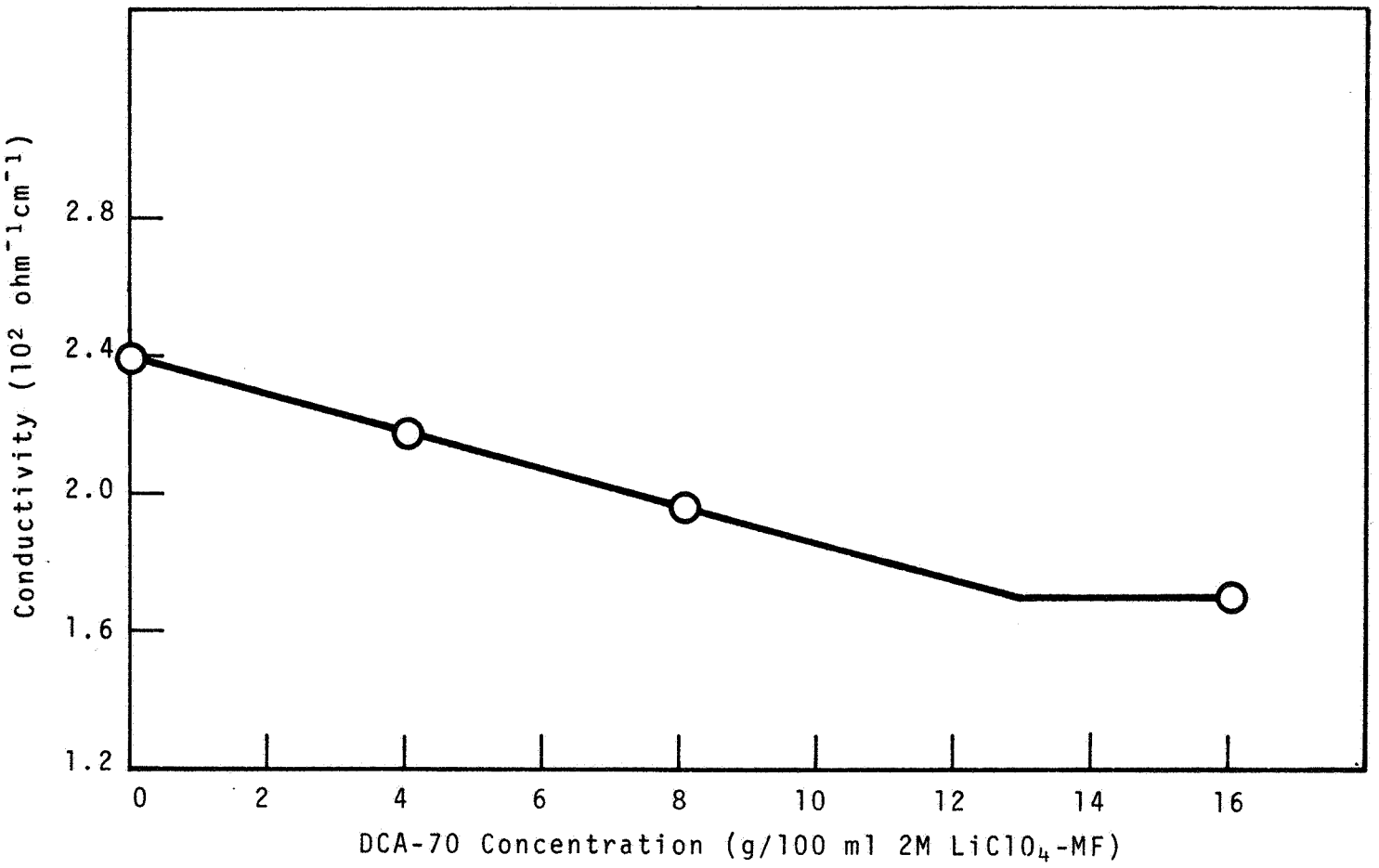


Figure 5. The Electrolytic Conductivity of 2M $LiClO_4$-MF Solutions Containing Various Concentrations of DCA-70

The solubility of LiCl in 2M $LiClO_4$(MF) was determined by saturating a solution with LiCl, filtering, diluting with water and titrating with standard $AgNO_3$ solution. A potentiometric endpoint was obtained, using a silver wire and saturated calomel electrode. The solubility is 5.2 g/ℓ or 0.12 molar. In pure solvent (MF) the solubility of LiCl is 1.1 g/ℓ.

2. $LiAsF_6$-Methyl Formate Electrolyte

a. Preparation of $LiAsF_6$ and Electrolyte Characterization

Based on the results obtained at Honeywell (ref. 4), $LiAsF_6$ was prepared in methyl formate solution by precipitation of KBF_4 from stoichiometric equivalents of $LiBF_4$ and $KAsF_6$ in methyl formate.

The $KAsF_6$ (Ozark-Mahoning) was dissolved in purified methyl formate to give the correct molarity. $LiBF_4$ (Foote Mineral Co.) was then added to this solution in stoichiometric equivalence. After 30 minutes the solution was filtered to remove the KBF_4. All operations were performed in a glove box.

Solutions of 2 and 3 molar $LiAsF_6$ were prepared in this manner. Density and conductivity data are given in Table 3. The density was determined with a Lipkin bicapillary pycnometer.

Table 3

PROPERTIES OF $LiAsF_6$ (MF) Electrolytes

Molarity (moles/l)	Density (g/ml)	Conductivity (ohm^{-1} cm^{-1})
2	1.22	3.9×10^{-2}
3	1.24	3.8×10^{-2}

The conductivity and density of these solutions are surprisingly similar. The conductivities of the solutions are similar to those in reference 4, although our 3M value is higher.

b. Constant Current Discharge Data

Cells were discharged with 2M and 3M $LiAsF_6$ at 10 and 25 mA/cm^2. Cells 110717 and 110723 would not operate with 1.5 ml of electrolyte; therefore, the cells were dismantled and 0.3 ml more was added. There is considerable evaporation loss using this procedure and the energy density values are adversely effected. The data (Table 4) show a voltage improvement for $LiAsF_6$ over $LiClO_4$. However, there is no increase in efficiency, or ability to discharge at a higher rate, due to this electrolyte change. The higher electrolyte conductivity [0.039 vs 0.024 mho/cm for $LiClO_4$ (MF)] improves the conduction within the cathode, thus decreasing the IR loss and increasing the average voltage. However, this increased conductivity does not allow a faster or more efficient discharge. Hence, these discharge factors are apparently not limited by ionic mobility. It also seems unlikely that the factors are limited by simple DCA-70 diffusion, since the DCA-70 solubility is 15 wt-%. However, the controlling factor may be diffusion or migration through insoluble reaction product layers.

Table 4

A COMPARISON OF $LiAsF_6$ AND $LiClO_4$ AS ELECTROLYTE SALTS IN THE Li/DCA-70 CELL

Cell	Electrolyte	Current Density (mA/cm^2)	Ave. Voltage (v)	Efficiency (%)	Energy Density (w-hr/lb)
110720	2M $LiAsF_6$	10	3.21	51	146
110718	2M $LiAsF_6$	25	2.99	8	25
110722	3M $LiAsF_6$	10	3.28	52	153
110723	3M $LiAsF_6$	25	3.33	11	32
109314	2M $LiClO_4$	10	2.77	52	133
109304	2M $LiClO_4$	25	2.78	11	28

B. CATHODE INVESTIGATIONS

1. Decomposition of DCA-70 in Methyl Formate and 2M $LiClO_4$-Methyl Formate Solution

a. Introduction

In order to obtain thin layers of DCA-70 for reduction efficiency studies (see Section II.B.2) solution deposition investigations were carried out. The deposition of DCA-70 from solution onto the conduction substrate was found to be more complex than originally anticipated. The most logical candidate solvent was methyl formate, the low boiling liquid that is the electrolyte solvent in our Li/DCA-70 cells. In previous work (ref. 1), we determined that the solubility of DCA-70 in methyl formate was approximately 14%. When an attempt was made to prepare a 10% solution for deposition studies, it appeared that a 2 to 3% solution was saturated. Titration of active chlorine in the supernatant liquid indicated that, even though there was undissolved solid (indicating saturation), all of the active chlorine was in the supernatant liquid. In addition, when more DCA-70 was added, almost all the added active chlorine was present in the liquid, even though the amount of solid in the solution increased. The active chlorine completely disappeared from the stoppered volumetric flask over a 24-hour period with the generation of HCl and a second white precipitate.

Similar results were found upon the addition of DCA-70 to 2M $LiClO_4$-methyl formate electrolyte solutions. Since the decomposition of DCA-70 by methyl formate might be a cause for reduced cathode efficiencies, a limited program was undertaken in order to determine the nature of the reaction.

b. Decomposition of DCA-70 in MF Solutions

(1) Solubility in MF (No Electrolyte Salt Present)

Figure 6 shows the determination of DCA-70/MF solubility by active chlorine titration of the supernatant liquid. Although some insoluble solid is present at 2%, true saturation occurs at approximately 15%.

(2) The Rate of DCA-70 Decomposition in MF

As shown in Figure 6, approximately 15% DCA-70 (3.0 meq/ml) is required to saturate methyl formate. The apparent saturation point, however, is much lower [2%(0.4 meq/ml)].

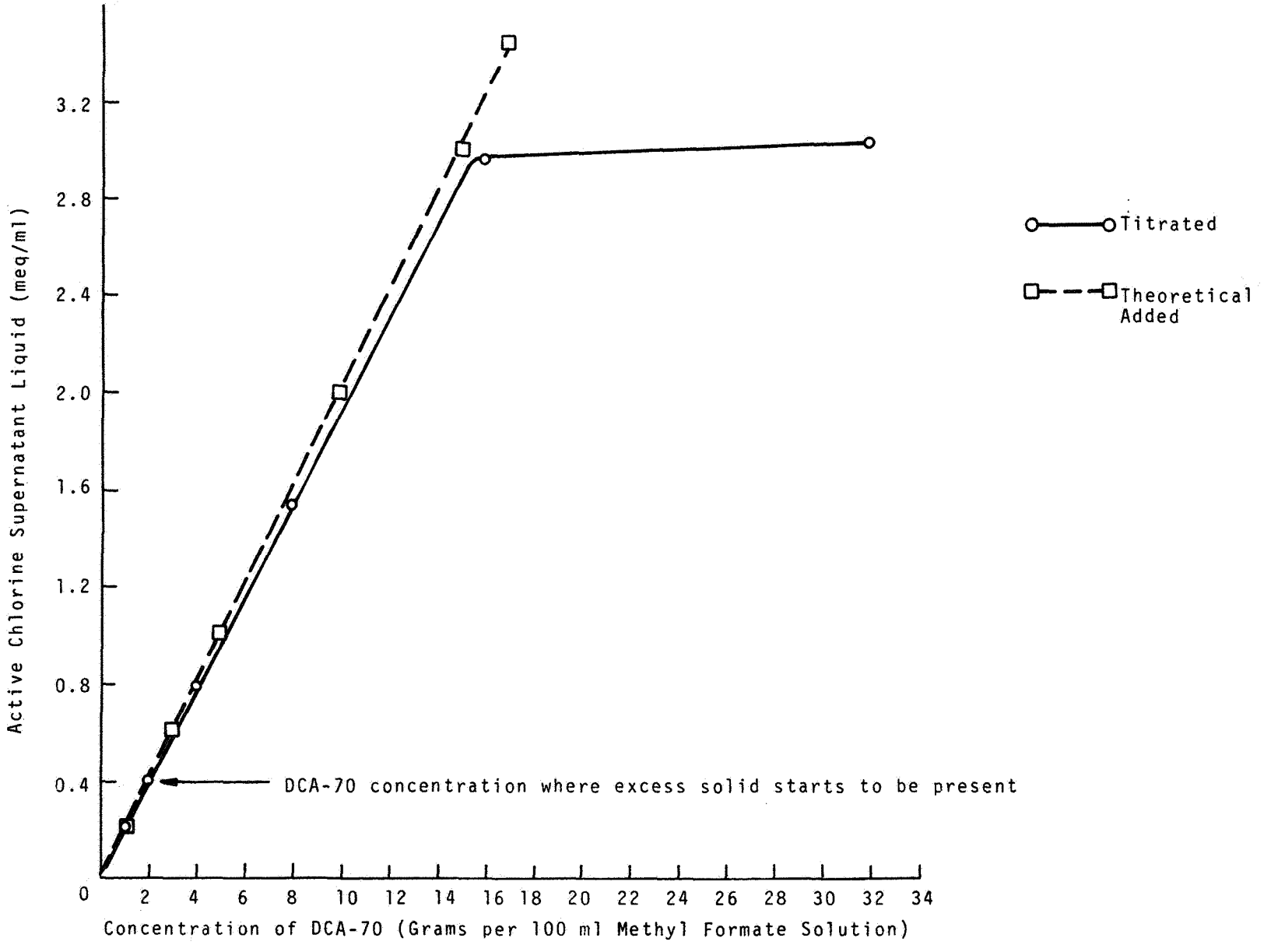


Figure 6. The Solubility of DCA-70 in Methyl Formate

A study of the rate of decomposition of DCA-70 in our standard methyl formate at two different concentration was undertaken (Figure 7). The decomposition is rather slow at first and then becomes more rapid. The data are similar to what might be expected from a second order autocatalytic reaction (ref. 5). Since we felt that this depolarizer decomposition might constitute a serious battery problem, we investigated the cause of the reaction.

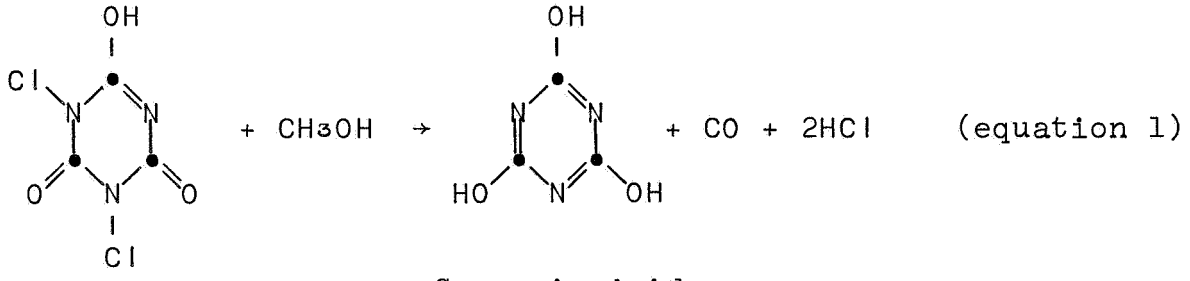
(3) Cause of DCA-70 Decomposition

Vapor phase chromatographic (vpc) conditions were developed for the determination of impurities in methyl formate (3 ft. 1/4" Poropak, 50/80 mesh, Type Q, 150°C, 15 psi He).

MC & B "Spectroquality" methyl formate (MF) showed 96.1% MF, 3.8% methanol and 0.1% water. Formic acid and formaldehyde, if present, were not determinable, since they respectively, have the retention times of MF and methanol.

The methyl formate used for our electrolyte solutions in high energy battery tests normally was allowed to stand over 4A molecular sieves, and then distilled to remove the sieves. Vpc analysis showed that this material had a decomposition similar to the untreated MF.

Since alcohols are known to be oxidized readily by DCA-70, methanol was the most logical choice as the factor causing the decomposition. A possible decomposition reaction is seen in equation 1.



DCA-70

Cyanuric Acid

At 15g DCA-70 per 100 ml MF solution (true saturation-see Figure 6), 3.04 ml of methanol (7.6×10^{-2} mole) is required to reduce all the DCA-70 added. As stated above, 3.8 ml of methanol are available in solution. In addition, if an equal amount of formic acid is present (equation 2), but undetected because of its vpc characteristics, only 2.03 ml of methanol would be required to decompose all the DCA-70 present in a saturated solution.

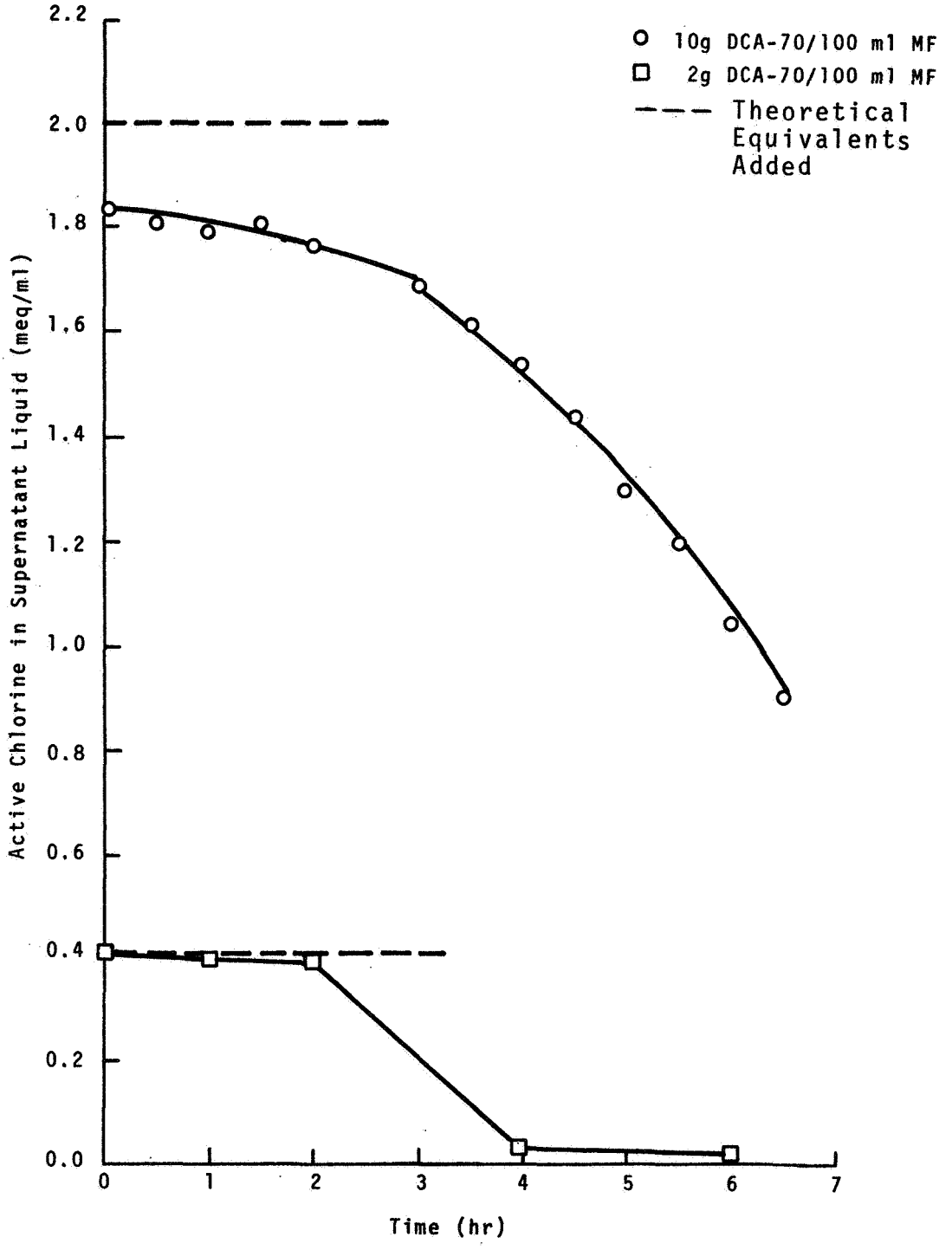
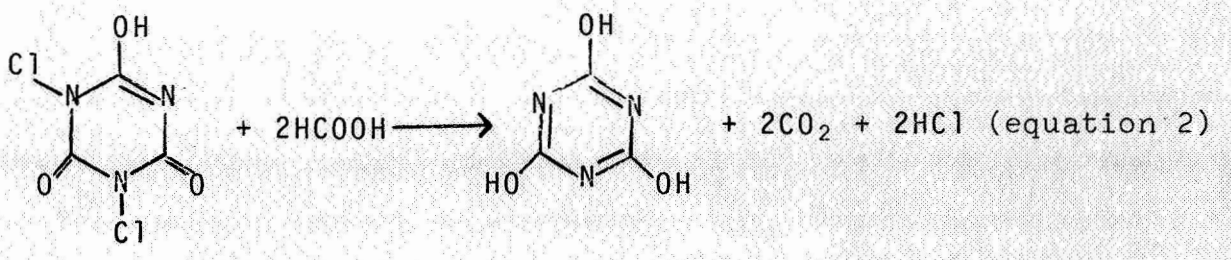
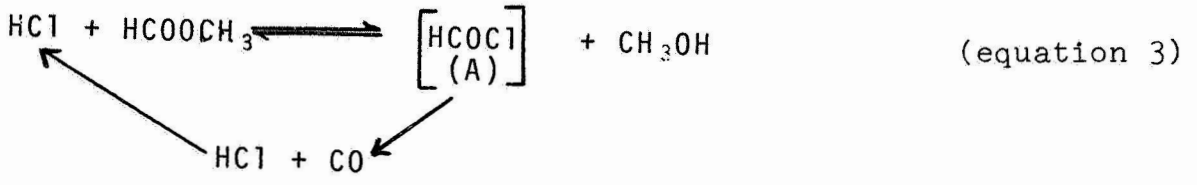


Figure 7. The Rate of DCA-70 Decomposition in Standard Methyl Formate.



While these proposed reactions might have second order rates, the apparent autocatalytic nature of the observed reaction needs further explanation. It is observed that in both equation (1) and (2), HCl is liberated. This is observed under experimental conditions. If HCl reacted with the solvent, methyl formate, as in equation (3), then the concentration of methanol would continually increase during the course of the reaction.



(equation 3)

Since at least 2 moles of HCl are produced for every mole of methanol consumed [equation (1)] the methanol concentration from the hydrochlorysis of MF should continually increase. In addition, the HCl produced acts only as a catalyst for the decomposition of MF, since the formyl chloride (A) produced is unstable and disproportionates into HCl and carbon monoxide. The proposed scheme, equations (1), (2) and (3) offers an explanation for the apparent second order autocatalytic nature of the reaction.

(4) Removal of Methanol from Methyl Formate

Numerous attempts to remove the 4% methanol present in MF were unsuccessful. The technique normally used for drying MF prior to electrolyte preparation (stand over 4A molecular sieves and distill) did not remove methanol. Neither did careful fractional distillation (Table 5).

Table 5

THE EFFICIENCIES OF VARIOUS TECHNIQUES FOR METHANOL REMOVAL FROM METHYL FORMATE

Technique	Remarks
Distillation	
50 cm Vigreaux column	Methanol content not reduced
Adsorption Chromatography	
Silica gel	No methanol removal
5A and 13X molecular sieves	Poor methanol removal
4A molecular sieves	Good methanol removal (from 3.7% to 0.1%)
$MgSO_4$	No methanol removal
Chemical Reaction	
CaH_2	Methanol reduced by 20%

Column chromatography through 4A molecular sieves (75 g/250 ml, 1 in. diameter column, stand time 0.5 hrs., removal rate 3 ml/min) proved best. Methanol was reduced from 3.8% to 0.1%. Rechromatography over fresh sieves did not reduce the vpc peak further. It is possible that the 0.1% is formaldehyde rather than methanol, since both compounds have the same retention time under our vpc conditions.

(5) Effect of Methanol Removal on the Decomposition of DCA-70 in Methyl Formate

A comparison of the decomposition rates of DCA-70 in standard and purified (4A molecular sieve treatment) methyl formate is shown in Figure 8. Purification decreases the decomposition rate of a 2% solution by at least a factor of ten.

(6) Summary

DCA-70 decomposes in methyl formate solution.

The decomposition is caused by an impurity in the MF (4% methanol).

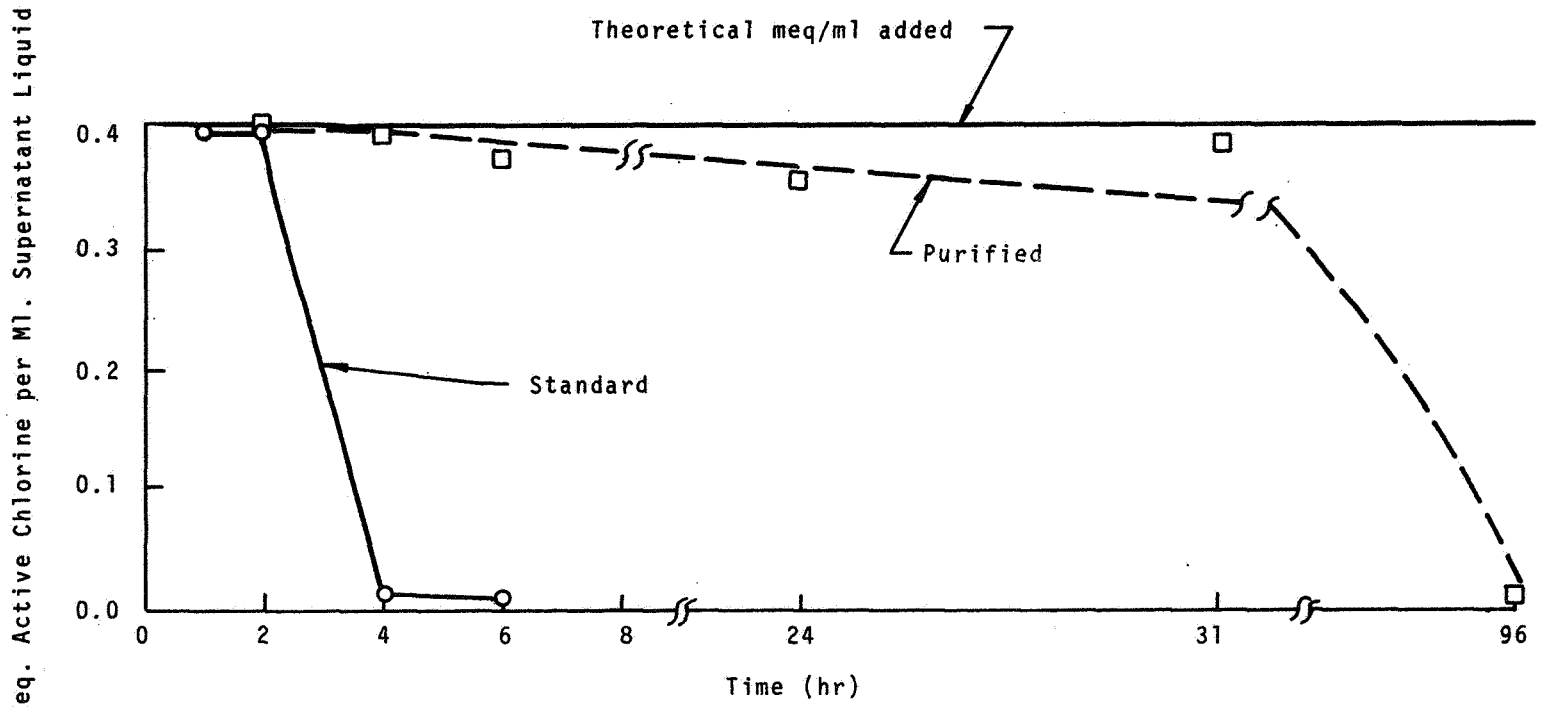


Figure 8. The Effect of Methanol Removal on the Decomposition of DCA-70 in Methyl Formate (2.0g/100 ml)

Methanol can be removed from MF by chromatography over 4A molecular sieves.

Questions which required further study were:

Did DCA-70 decompose in our standard electrolyte solution (i.e., with $LiClO_4$ present)?

What is the decomposition product of DCA-70 in MF? Is it associated with cathode limitation problems?

b. Decomposition of DCA-70 in $LiClO_4$-MF Electrolyte Solutions

(1) Solubility of DCA-70 in 2M $LiClO_4$-MF Solutions

The solubility of DCA-70 in electrolyte (ca. 13%) is similar to that in MF alone. The point of apparent saturation is higher, however (Figure 9).

(2) The Effect of $LiClO_4$ on the Decomposition of DCA-70 in Standard Methyl Formate

The addition of 2M $LiClO_4$ to standard (unchromatographed) MF caused a large decrease in the rate of decomposition of DCA-70 relative to MF alone (Figure 10). Thus, at a concentration of 10% DCA-70, the presence of 2M $LiClO_4$ reduced DCA-70 decomposition to a level comparable to that of DCA-70 in MF chromatographed over 4A molecular sieves (see Figure 8). With $LiClO_4$ present, only 5% DCA-70 decomposition took place after 24 hours. Without $LiClO_4$ present, the DCA-70 is completely decomposed after the same time period.

Although $LiClO_4$ stabilizes DCA-70 solutions in standard MF, the stabilization is even greater if the $LiClO_4$ is used in purified MF. This is especially noticeable at low DCA-70 concentrations. This effect in 2% DCA-70 solutions is shown in Figure 11.

All of the above DCA-70 decomposition experiments were carried out at DCA-70 to $LiClO_4$-MF electrolyte solution ratios of 1:50 (2%) or 1:10 (10%). The DCA-70 to electrolyte solution ratio in our high energy density battery cells is 1:1 (ref. 1). When DCA-70 decomposition was studied at this high concentration, there was essentially no decomposition in either purified or standard electrolyte solution (Figure 12).

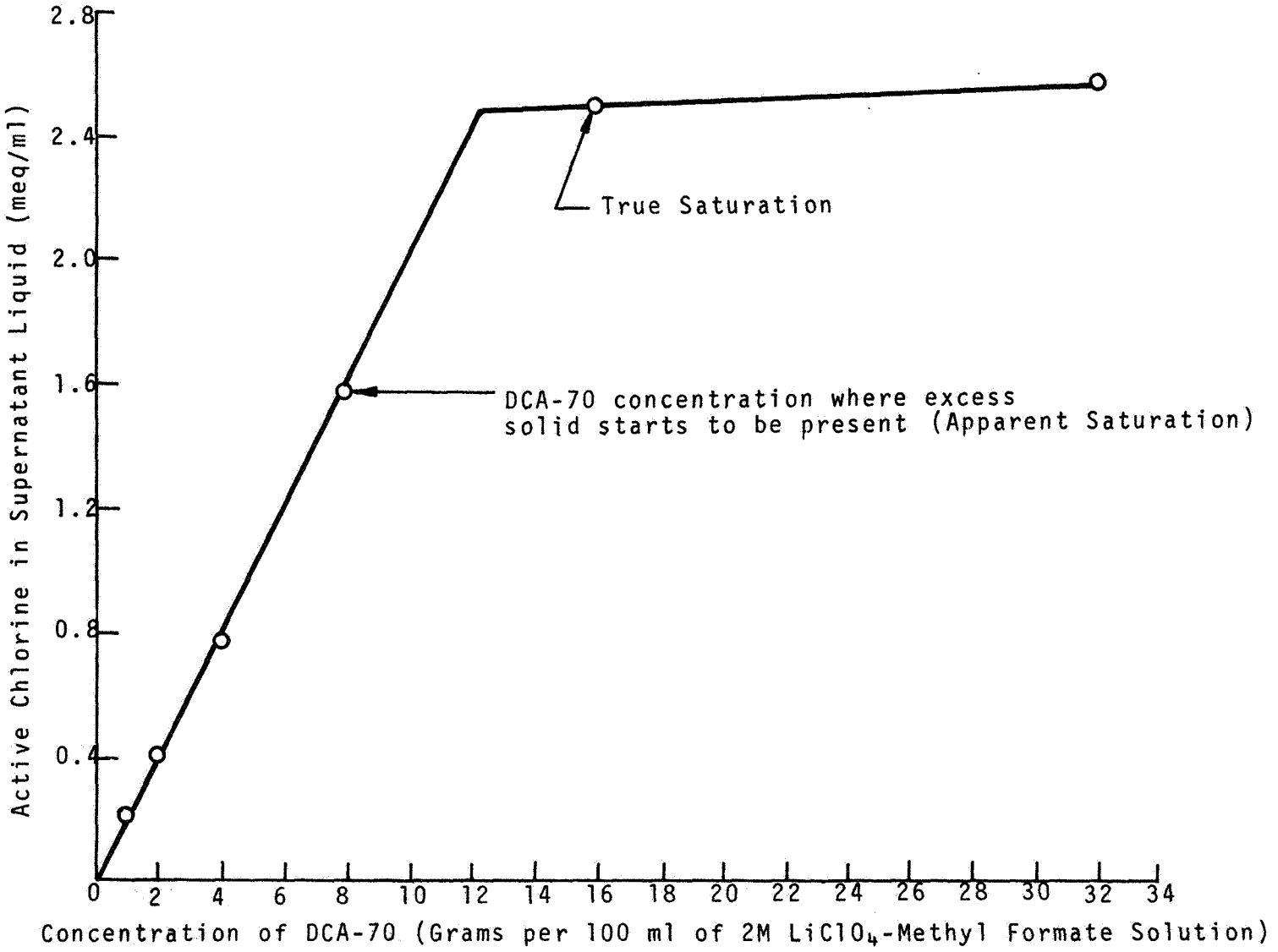


Figure 9. The Solubility of DCA-70 in 2M $LiClO_4$-Methyl Formate Solution

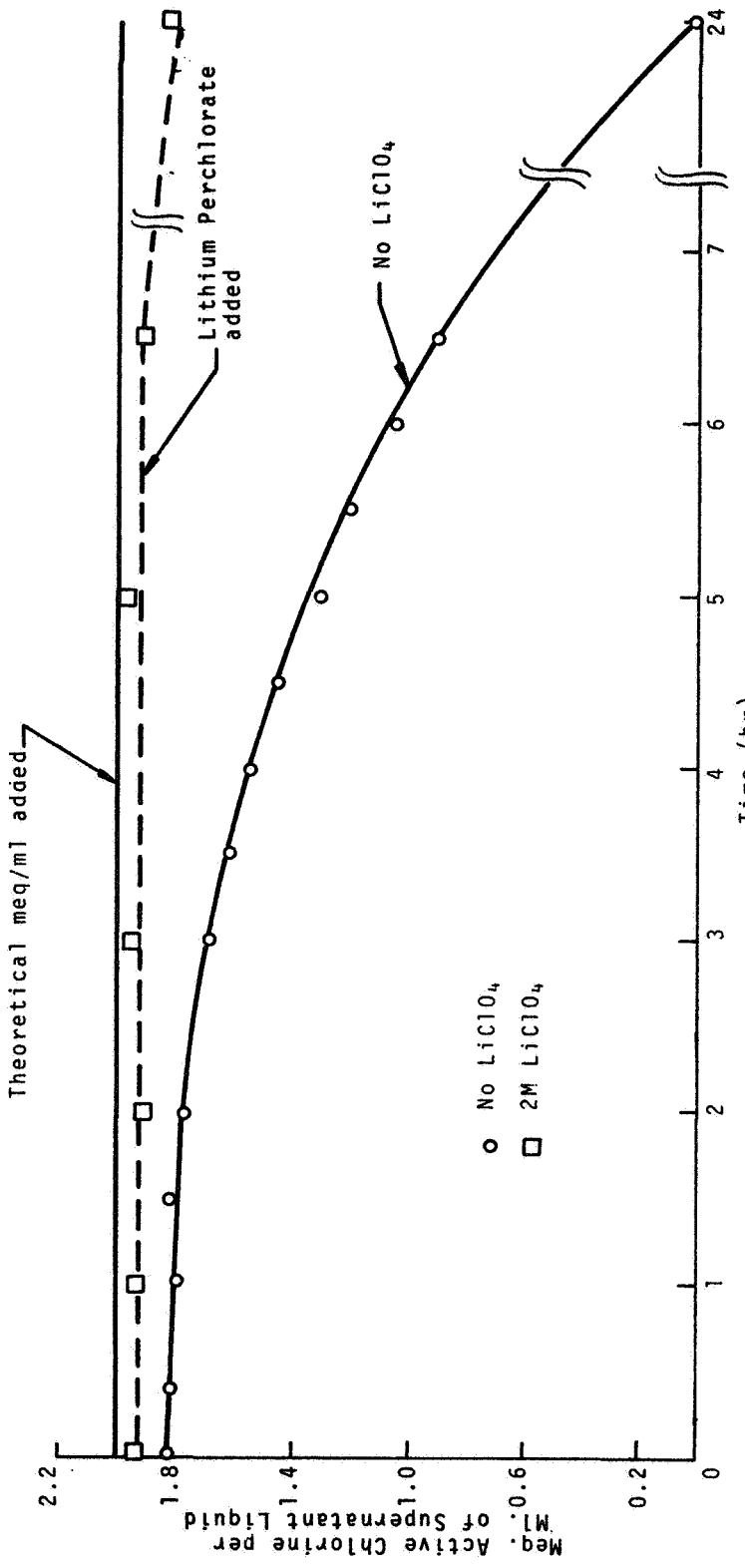


Figure 10. The Effect of $LiClO_4$ on the Decomposition of DCA-70 in Standard Methyl Formate (10 g DCA-70/100 ml MF)

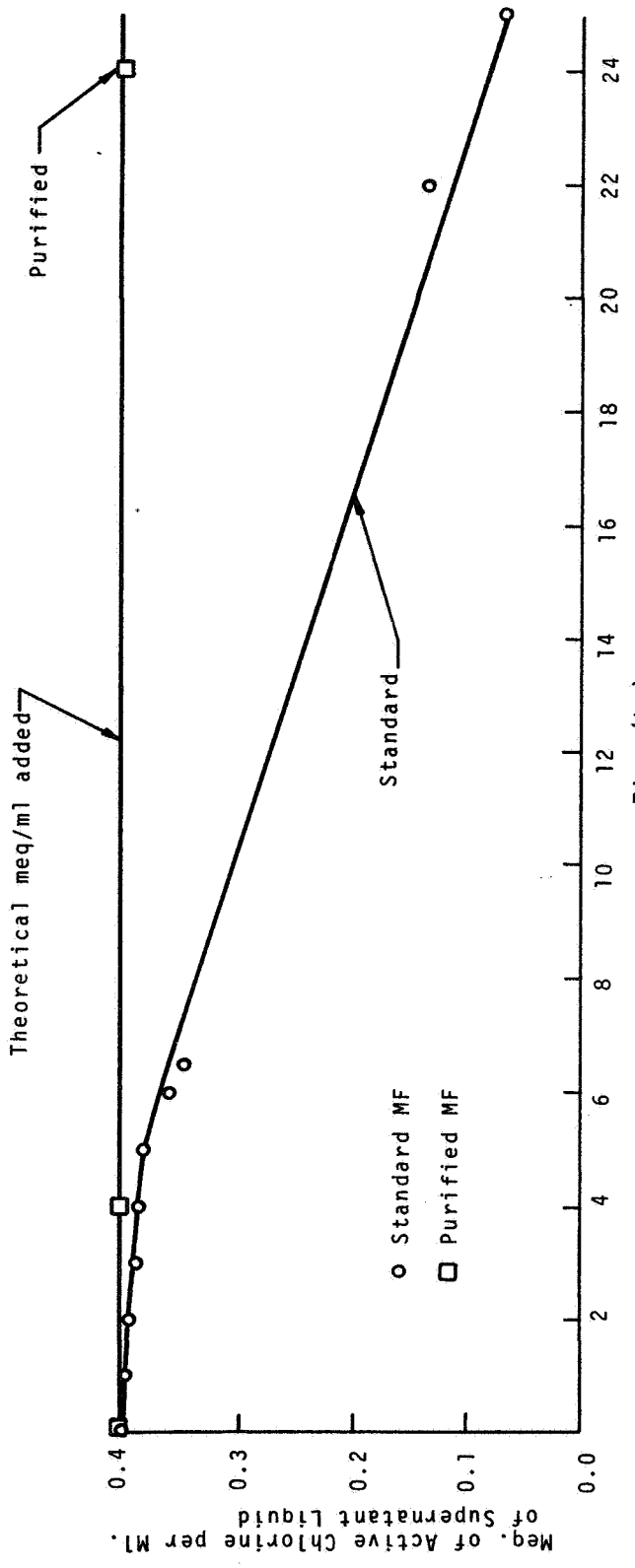


Figure 11. The Effect of Using Purified Methyl Formate on the Decomposition of DCA-70 in 2M $LiClO_4$ Electrolyte (2.0 g/100 ml)

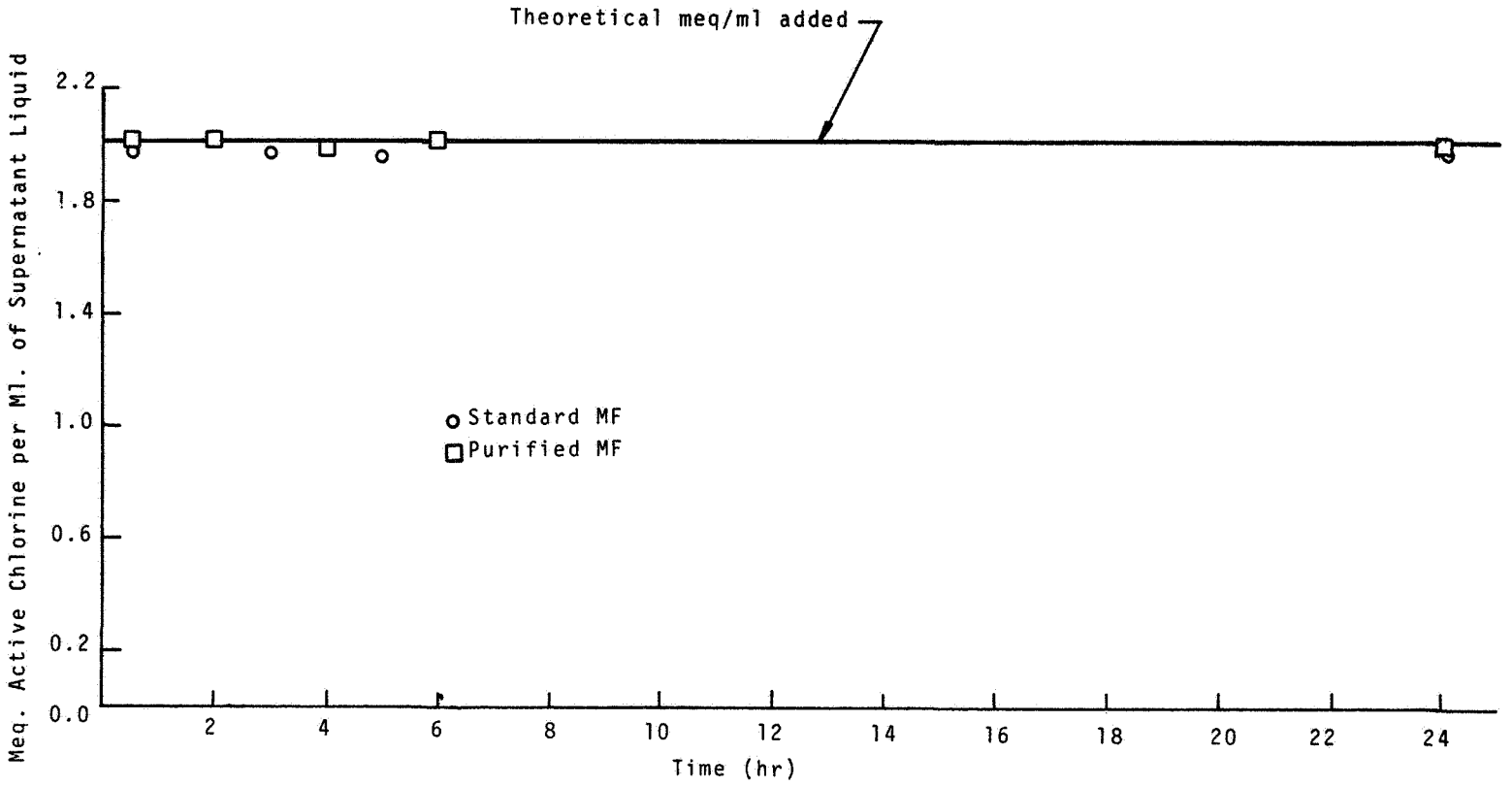


Figure 12. The Effect of Using Purified Methyl Formate on the Decomposition of DCA-70 in 2M $LiClO_4$ Electrolyte (100 g/100 ml, the battery cell concentration)

d. Identification of the Decomposition Products of DCA-70 in MF

(1) Quantitative Analysis of the Decomposition of DCA-70 in Standard MF

As described above, excess solid (and apparent saturation) occurs in DCA-70/MF solutions starting at approximately 2% DCA-70. In addition, after standing for 24 hours, the DCA-70 solutions contain a white solid containing no chlorine. The question we set out to answer was: What are the initial and final white solids?

One gram samples of DCA-70 were diluted with standard (unpurified) MF in 10 ml volumetric flasks at room temperature (22°C). The samples were inverted 25 times during the first minute after MF addition. At the end of the specified times, the solid in the flask was isolated by vacuum filtration, weighed and titrated for active chlorine content. The filtrates from the volumetric flask were evaporated to dryness, and the resulting solid weighed and titrated for active chlorine content. The results are shown in Table 6. The data indicate:

Undissolved Solid

About 10% of the initially added DCA-70 is insoluble, and this percentage remains constant for at least 2 hours. Sometime between 2 and 4 hours a change occurs. Most of the solid goes into solution and the ACL number of the undissolved material decreases. After 24 hours, a new product, more insoluble than DCA-70, has been formed. This material has a low chlorine content and an ACL No. of 7.

On the basis of subsequent studies, (see Section II.D), the insoluble active chlorine compound making up 10% of the DCA-70 sample is DCA-60, the sodium salt of DCA-70.

Solid from Evaporation of the Supernatant Liquid

Approximately 85% of the initially added DCA-70 goes into solution. The weight of material in solution increases with time as the undissolved solid (DCA-60) slowly goes into solution. The ACL No. stays fairly constant for 2 hours and then decreases. After 24 hours, almost all the dissolved material has been changed to the insoluble white solid, which has a very low active chlorine content. Useful information can be obtained from a comparison of the milliequivalents of active chlorine per milliliter of supernatant liquid in Table 6 and Figure 10 (two different experiments). These data show that similar values are obtained from the titration of an aliquot of supernatant liquid and the titration of the

Table 6

QUANTITATIVE ANALYSIS OF THE DECOMPOSITION OF DCA-70 IN STANDARD METHYL FORMATE
(1.000 g/10.0 ml, 20.2 meq. Active Chlorine Theoretical)

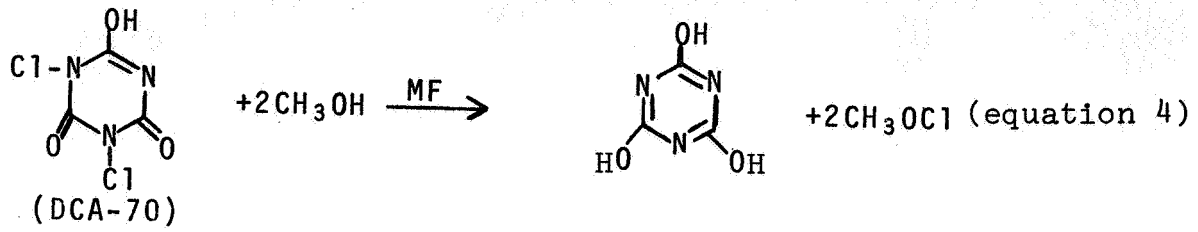
Time (hr)	Undissolved Solid					Solid From Evaporation of Supernatant Liquid					Total Recovery			
	Weight		Active Chlorine			Weight		Active Chlorine			Weight		Active Chlorine	
	g	%*	meq.	%†	ACL No.	g	%	meq.	%	ACL No.	g	%	meq.	%
0.06	0.114	11	2.05	10	64	0.849	85	15.0	74	64	0.963	96	17.1	85
0.5	0.112	11	2.18	11	69	0.857	86	17.3	86	68	0.969	97	19.5	96
1.0	0.074	7	1.24	6	59	0.859	86	16.3	81	68	0.933	93	17.5	87
2.0	0.082	8	1.38	7	60	0.873	87	16.3	81	65	0.955	95	17.7	88
4.0	0.041	4	0.38	2	32	0.908	91	15.0	74	58	0.949	95	15.4	76
24.0	0.687	68	1.34	7	7	0.042	4	0.0	0	0	0.729	73**	1.3	6

* Percent of 1.000 g DCA-70 initially added.

† Percent of 20.2 meq. active chlorine initially added.

** 65 Weight % expected on conversion of DCA-70 to cyanuric acid.

solid obtained after vacuum evaporation of the supernatant liquid solvent (i.e., MF). This indicates that the oxidizing agent in the supernatant liquid is DCA-70 or some similar non-volatile product, and not methyl hypochlorite (b.p. 12°C) formed from the reaction in equation (4),



since CH_3OCl would have evaporated with the MF.

Total Recovery of Initially Added DCA-70

The total recovery of "grams added" stays quite constant up to 4 hours. It decreases to 73% after 24 hours. If all the DCA-70 were converted into cyanuric acid plus products which were volatile under the vacuum isolation conditions (e.g., HCl, HCHO, CO_2, $COCl_2$, CO), then a 65% recovery would be expected.

(2) Structural Analysis of the Insoluble White Precipitate

As seen in Table 6, DCA-70 is converted to an insoluble white solid, mp>360°C, upon exposure to standard MF for 24 hours. This solid contained very little chlorine (by $S_2O_3^{=}$ titration or Beilstein test). The infrared spectrum of the solid was similar to, but not identical with, cyanuric acid (Figure 13). Recrystallization of this solid from water gave cyanuric acid. A more important fact about this solid, however, is that its infrared spectrum is almost identical with that from the precipitate which coated our Pt test electrode during the electroreduction of dilute DCA-70/MF solutions (see Section II.C, and Figure 14). This solid might be responsible for reduced cathode efficiencies in full cell discharges.

The amount of material obtained in the Pt electrode studies was very small (< 5 mg) so that only a semi-quantitative lithium analysis was possible. Lithium, probably as LiCl, was present in > 10% concentration.

The elemental analysis of the insoluble, reduced precipitate (57849a), obtained from DCA-70 in MF (no $LiClO_4$) is compared with that of cyanuric acid in Table 7.

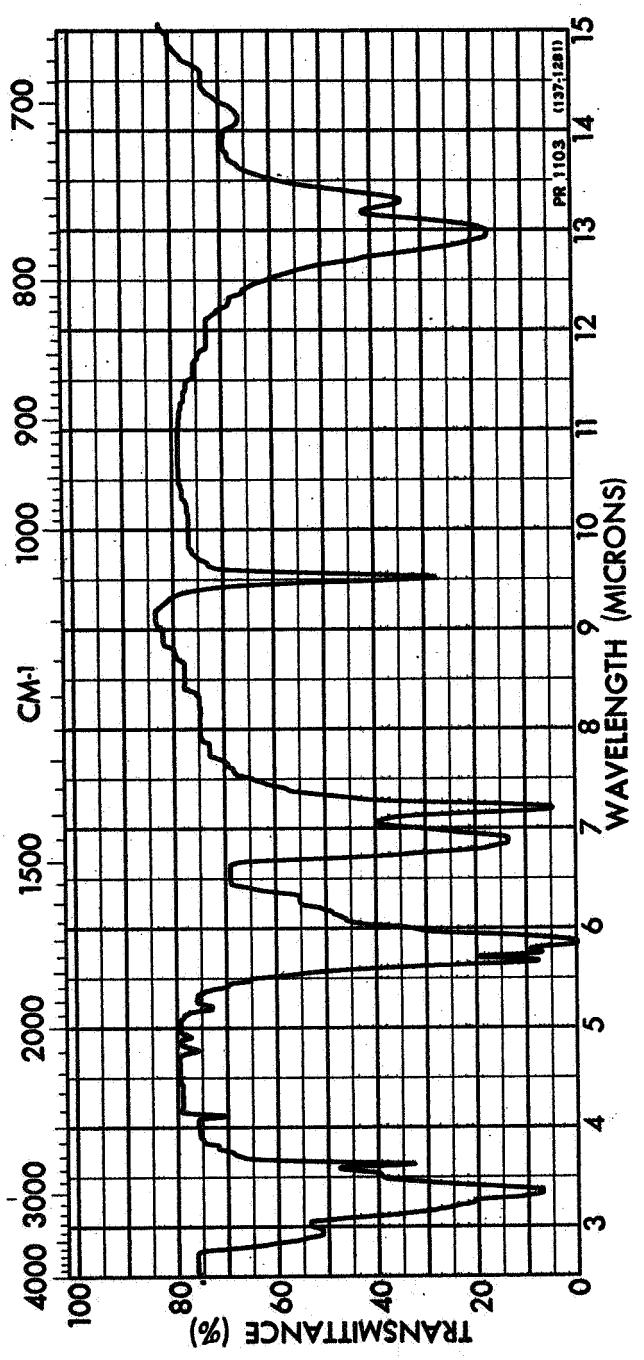


Figure 13a. DCA-70 Decomposition Product (KBr Pellet)

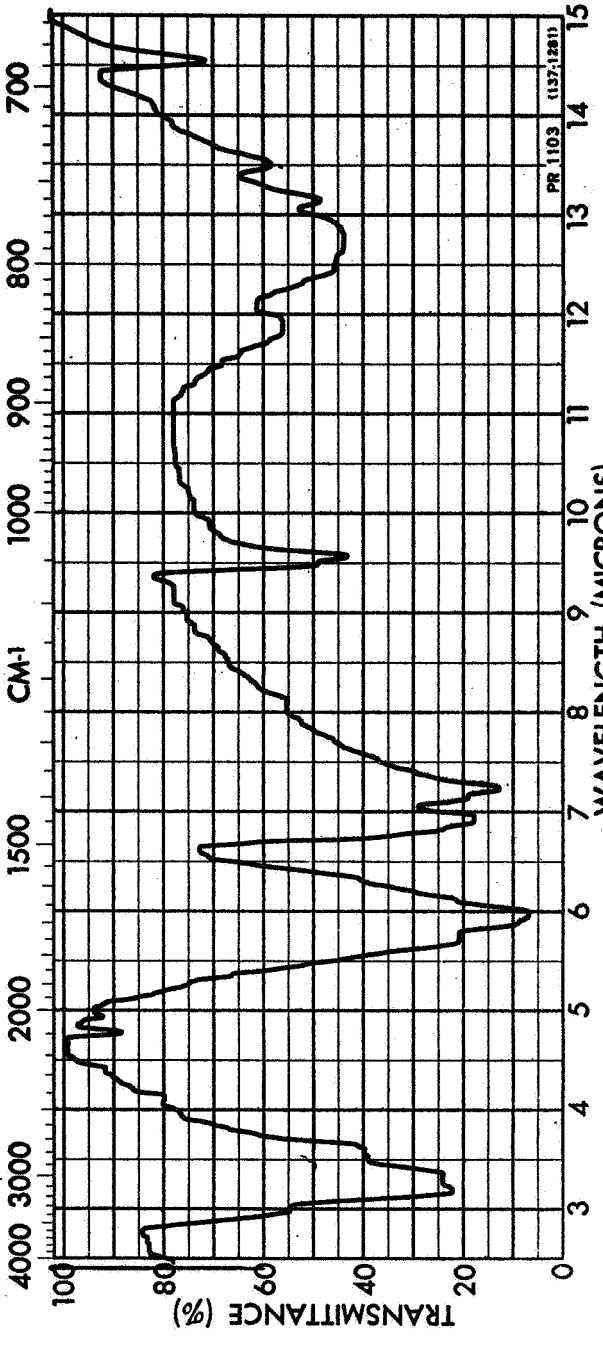


Figure 13b. Cyanuric Acid (KBr Pellet)

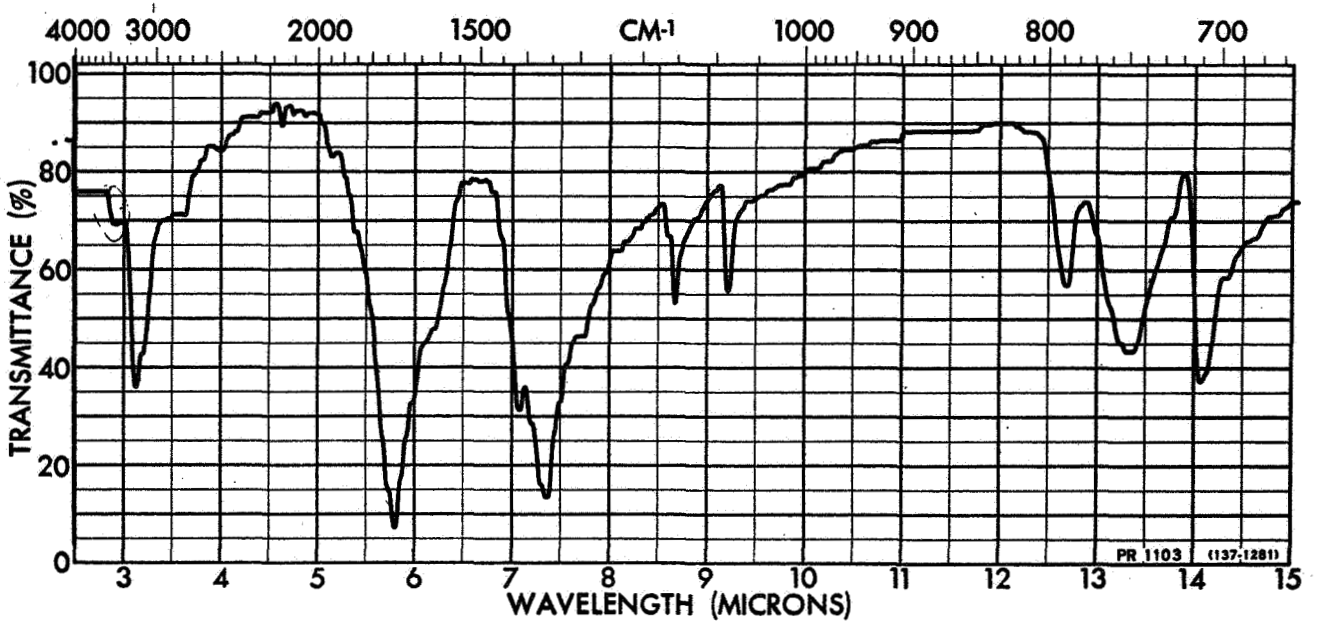


Figure 14a. DCA-70 (KBr Pellet)

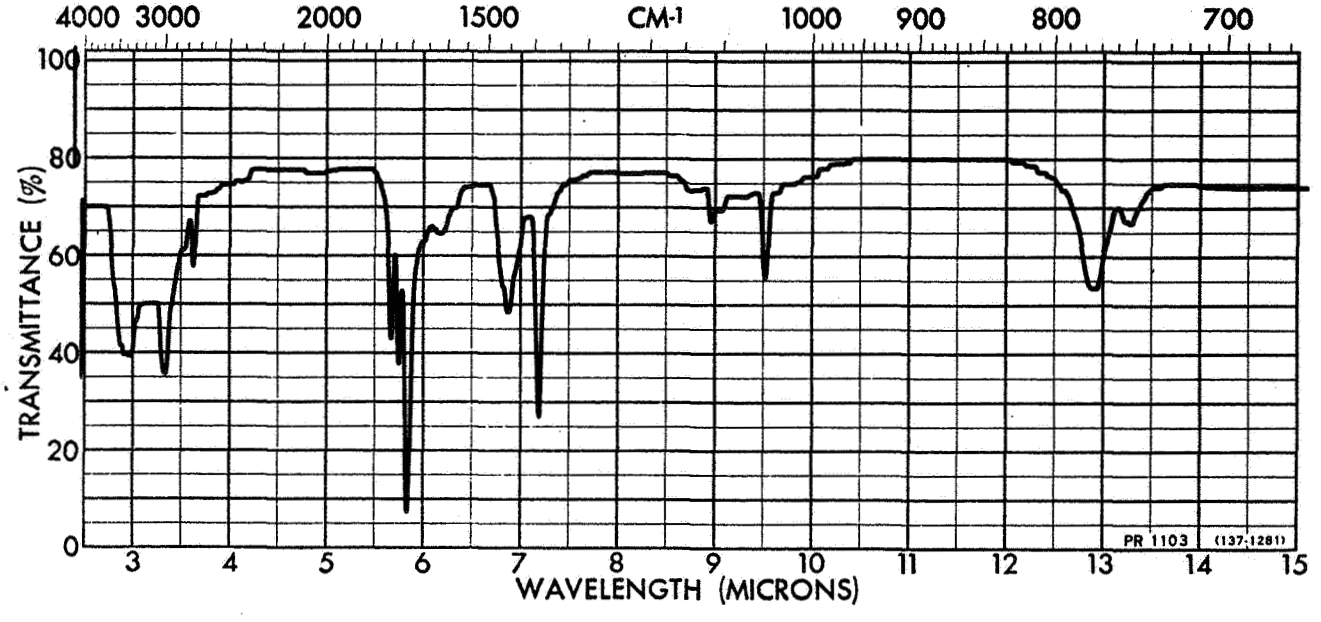


Figure 14b. DCA-70 Electro-reduction Product (KBr Pellet)

Table 7

ANALYSIS OF THE DCA-70/MF DECOMPOSITION PRODUCT

Elements	Calculated for Cyanuric Acid (%)	Found for 57849a (%)
C	27.91	27.65
H	2.32	2.42
N	32.56	30.86
O	37.21	37.33*
Cl	0.00	1.74
ash	0.00	0.00

*by difference

With the exception of some residual chlorine, the elemental analysis is very similar to that expected for cyanuric acid. The infrared spectra were also similar, but not identical. While it is not possible to definitely assign a structure to 57849a, we can conclude the following:

57849a is organic and very similar to cyanuric acid.

The electrode precipitate contains an inorganic (> 10% Li), and an organic component. The organic component is the same as 57849a.

e. The Effect of Methyl Formate Purification on Cell Discharge

Table 8 shows that the removal of the methanol impurity from MF does not significantly alter the performance of the Li/DCA-70 cell. A difference in the amount of cell gassing did occur, however. This is discussed further in Section II,D.

2. DCA-70 Thin Layer Discharge

a. Introduction

In an effort to determine the optimum depolarizer-to-carbon ratio in the cathode mix, a program was devised in which the coulombic reduction efficiency of depolarizer layers would be measured as a function of layer thickness. In this way, the maximum thickness of active chlorine compound that can be discharged at 95% cathode efficiency was to be determined. Thin layers of MnO_2 have been studied previously (refs. 17, 18).

Table 8

DISCHARGE OF Li/2M $LiClO_4$(MF)/DCA-70 CELLS

Electrolyte Type	Load (ohms)	Discharge Time to 2v (min)	Average Voltage (volts)	Cathode Efficiency (%)	Energy Density (wh/lb)
Standard	30	285	3.13	64.4	192
Purified	30	286	3.12	63.3	188
Purified	9	77	2.85	51.4	139
Purified	124	1040	3.17	57.7	174
Standard (1) (2)	9	72	3.07	63	140
Standard (1)	8	108	2.73	49	128
Standard (1) (3)	124	1090	3.21	58	176

(1) Reference 1

(2) 1.0 g DCA-70

(3) 1.5 ml Electrolyte

b. Thin-layer Discharge Apparatus

The apparatus shown in Figure 15 was designed and constructed. Electrode testing was carried out in the following manner:

a. A thin layer of active chlorine compound was deposited on the surface of the test electrode.

b. The test electrode was inserted into the test apparatus.

c. The electrolyte level was raised with the leveling bulb until it contacted the electrode surface. The electroreduction began as soon as contact was made with the electrolyte.

The volume of the test cell was approximately 250 ml, and a Ag/AgCl reference electrode was used.

c. Test Electrode Preparation

Our test electrode is prepared by the deposition of a thin layer of DCA-70 onto a conducting, non-porous substrate.

Two completely different types of conducting substrates were considered: (1) platinum, and (2) carbon epoxy (ref. 6). Experimental tests were begun with the latter material since it was felt that it might better approximate our battery mix substrate.

Shell Epon Resin 820 and V-40 curing agent was mixed with Shawinigan acetylene black (SAB), and the mix was packed into a 1.0-cm diameter glass tube. After curing overnight, the electrodes were polished smooth on a Handimet grinder. A number of blends were tried before a satisfactory carbon epoxy electrode was prepared.

The first electrode contained 25% SAB. A 0.12-inch thick sample had a resistance of 7000 ohms. In another sample, the SAB was increased to 40%, and acetone was added to the mix to make it easier to work with. After several modifications, resistances of 5 ohms were obtained. The major change consisted of the fabrication of a Teflon holder for the epoxy mix containing a copper insert for better mix contact.

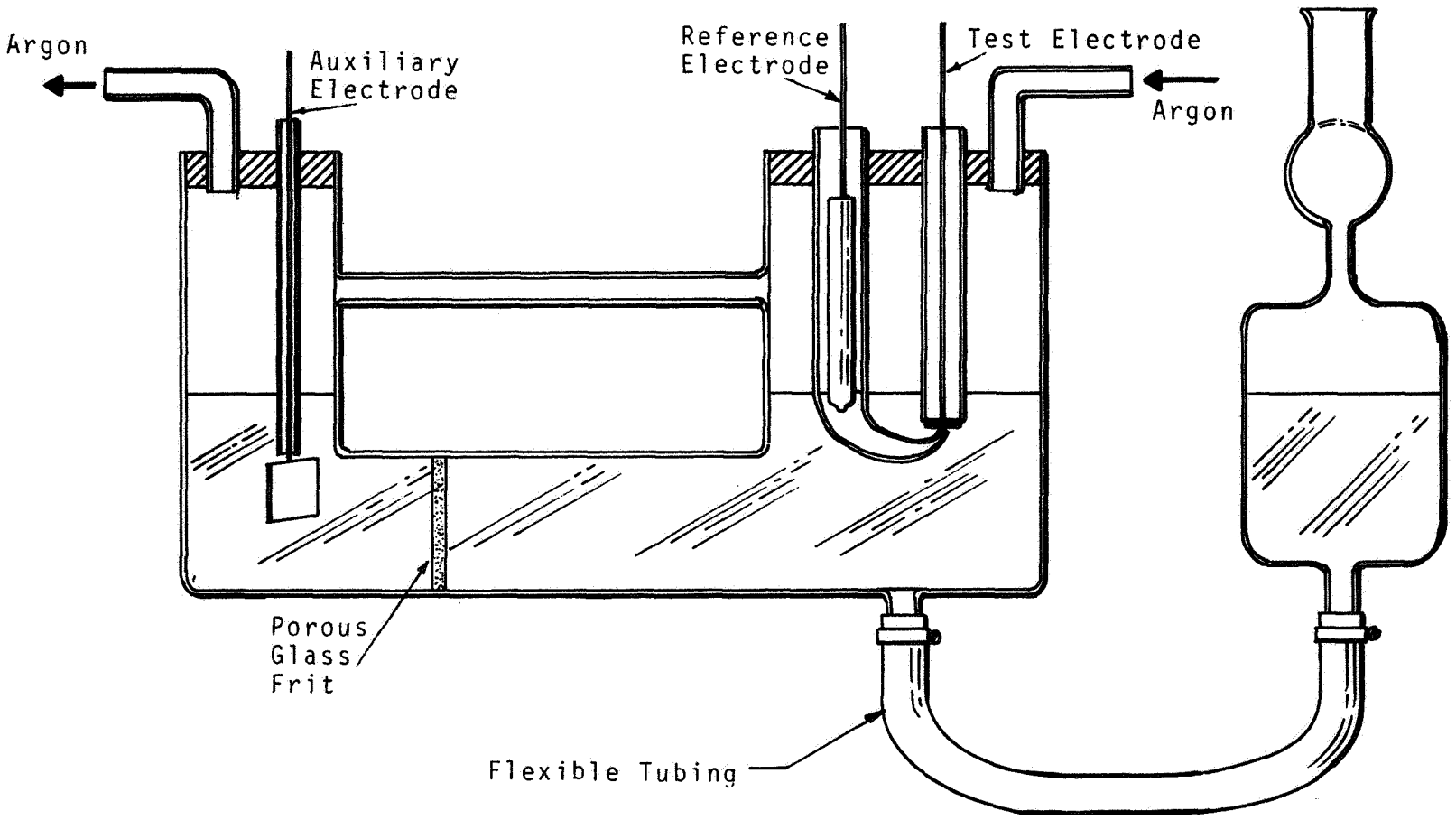


Figure 15. Test Cell for Depolarizer-Substrate Layer Testing

d. DCA-70 Thin Layer Deposition

Because of the uncertainties involved with deposition of DCA-70 films from methyl formate (see Section II,B,1), films were deposited from acetonitrile. By removing the acetonitrile without heat, under vacuum, relatively little DCA-70 decomposition occurred (Table 9). Most of the thin layers studied were prepared by this technique.

e. Discharge of DCA-70 Thin Layers

Preliminary discharge data indicated that very low coulombic efficiencies were being obtained. The solubility of the layers in the electrolyte was, therefore, investigated.

A deposit was evaporated from 0.1 ml of DCA-70 solution (10 mg/ml) in acetonitrile. Thus, 1 mg was deposited. This is equivalent to 1600 mA-sec (1.6 coulombs). This material, in a uniform thin layer, would be 5.6 microns ($\sim$ 0.0002 inch) thick. However, the actual coverage is $\approx$20% as observed by photomicrography. Deposited samples were immersed in 2M $LiClO_4$(MF) for specific time periods. When removed, the thin layer of electrolyte adhering to the electrode was allowed to dry and the amount of DCA-70 remaining on the electrode was determined by our standard $I_2/S_2O_3^=$ titration procedure. The results (Table 10) show that solubility, flaking, or decomposition is very rapid, compared to the time scale necessary for the electroreduction experiments.

Since active chlorine was found in the solution, the decomposition of DCA-70 can be eliminated as a cause for the rapid DCA-70 decrease. Since no flaking of DCA-70 crystals was observed for the acetonitrile-deposited layers, rapid solubility is most probably the major cause, although flaking cannot be ruled out completely. A layer of crystals deposited from a suspension of hexane did flake off, and no active chlorine was observed at the electrode after 15 seconds (Table 10).

The DCA-70 layers were deposited from acetonitrile and electroreduced under various conditions (Table 11). From this data it is evident that high currents and low layer capacities are necessary for best utilization. However, maximum utilizations were only $\sim$5%; the layers were very thin (2.8μ), and the current densities were high (1 mA/cm^2).

Using the carbon-epoxy electrode substrate (CEE), the electroreduction of DCA-70 could not be maintained at a current density of 1.0 mA/cm^2.

The high solubility of DCA-70 in our electrolyte made long term tests, i.e., > 5 minutes, impractical.

Table 9

PREPARATION OF DCA-70 THIN LAYERS
(1% Acetonitrile Solution)

Drying Method	% DCA-70 Undecomposed
Not dried	90
IR Lamp	0
Vacuum dry (20-60 min)	82-83

Table 10

THE SOLUBILITY OF DCA-70 LAYERS IN
2M $LiClO_4$-METHYL FORMATE

Electrolyte Contact Time (seconds)	Solvent Used in Layer Preparation	DCA-70 Remaining on Elec. mA-sec	%
0	AN*	1600	100
5	AN	590	32
30	AN	370	20
60	AN	180	6
120	AN	140	5
15	Hexane	0	0

* Acetonitrile

Table 11

ELECTROREDUCTION OF DCA-70 LAYERS (Area = 1 cm^2)

Calculated Layer Thickness (microns)	Layer Capacity (mA-sec)	Current (mA)	Electrode Type	OCP* (volts)	Electroreduction (mA-sec) above +0.5v	0.0v	-0.5v	Percent Utilization (>-0.5v)
5.6	1600	0.1	Pt	0.98	15	18	---	~1
5.6	1600	1.0	Pt	0.98	27	43	54	3.4
5.6	1600	2.0	Pt	0.96	40	60	80	5.0
2.8	800	1.0	Pt	0.90	17	37	51	6.5
5.6	1600	1.0	CEE**	0.50	0	2	9	0.6

* vs Ag/AgCl

** Carbon (SAB) Epoxy Electrode

To decrease the diffusion, and prevent any flaking of DCA-70, the electrode containing DCA-70 was covered with a polypropylene separator. The data of discharges with separator is shown in Table 12.

It is evident that separator does not solve the problem of diffusion, although efficiencies do increase by a factor of two. Depositing the DCA-70 from a hexane slurry was found to give results comparable to the acetonitrile solution deposition, whereas without the separator over the electrode, the hexane prepared layer flaked off the electrode and no electroreduction was possible.

One standard cathode mix section was placed on the platinum electrode, covered with a separator, and discharged. The current density was the same as above (1 mA/cm^2) but the weight of DCA-70 was about 60 times greater than used in the other thin layer studies. While discharge curve was flat (229 mA-min. above + 0.5V and 257 mA-min. above -0.5V vs. Ag/AgCl), the efficiency was only 13.5%. Although this is good compared to the pure DCA-70 thin layers, it is not comparable to the normal cell discharge efficiencies (60-70%). We attribute this to lack of pressure holding the SAB-DCA-70 layer against the platinum collector, and to excess electrolyte. Both too little pressure and too much electrolyte are known to be deleterious to total cell performance.

3. Cathode Blending Studies

a. Introduction

In order to more fully understand the physical nature of our DCA-70/carbon cathode mix, a program was initiated to study the effects of different blending techniques (fluff, shear) on the physical properties of the mix (conductivity, density, particle agglomeration and distribution). Bulk electronic conductivity was used to screen different mixes prior to full cell testing.*

b. Blending Techniques

(1) Waring Blender

A Waring blender with a Teflon coated blade was used as the normal mixing apparatus for the preparation of our DCA-70/Shawinigan acetylene black (SAB) cathodes. Mixing times with this apparatus must be kept to less than 10 minutes due to excessive heat generation. One to five gram samples were blended in this apparatus.

*Conductivity and compression of battery blacks have been measured previously (refs. 19, 20, 21) to study the structure of the black and of battery mixes.

Table 12

ELECTROREDUCTION OF DCA-70 LAYERS COVERED BY SEPARATOR (Area = 1 cm^2)

Calculated Layer Thickness (microns)	Layer Capacity (mA-sec)	Current (mA)	Electrode Type	OCP† (volts)	Electroreduction (mA-sec) above +0.5v	0.0v	-0.5v	Percent Utilization (>-0.5v)
11.8	3970	1.0	Pt*	0.77	52	135	150	3.8
3.9	1100	1.0	Pt**	0.79	18	69	91	8.3
7.8	2650	1.0	Pt*	0.91	74	132	147	5.5

* Deposited from a hexane slurry.

**Deposited from 1% acetonitrile solution.

† Vs. Ag/AgCl

(2) Ball Mill Blender

A small ceramic ball mill (375 cm^3), containing 18 two centimeter diameter stones, was used as our shear action blender. Ten to 25 gram samples were mixed.

(3) Patterson-Kelly Blender

Two one-pint, twin shell blenders were used as our fluff action blender. Twenty-five gram samples mixed with this blender.

c. Conductivity Apparatus

A cell for the measurement of cathode mix conductivity and density (as a function of applied pressure) was designed and constructed. This apparatus which was built to be used in a Carver press, is shown in Figures 16 and 17.

Conductivities were measured under ambient conditions in the pressure range 3.0-10,000 $lb/in.^2$. To protect the metal plunger from corrosion by DCA-70, the faces adjacent to the mix were rhodium coated.

d. General Conductivity Data

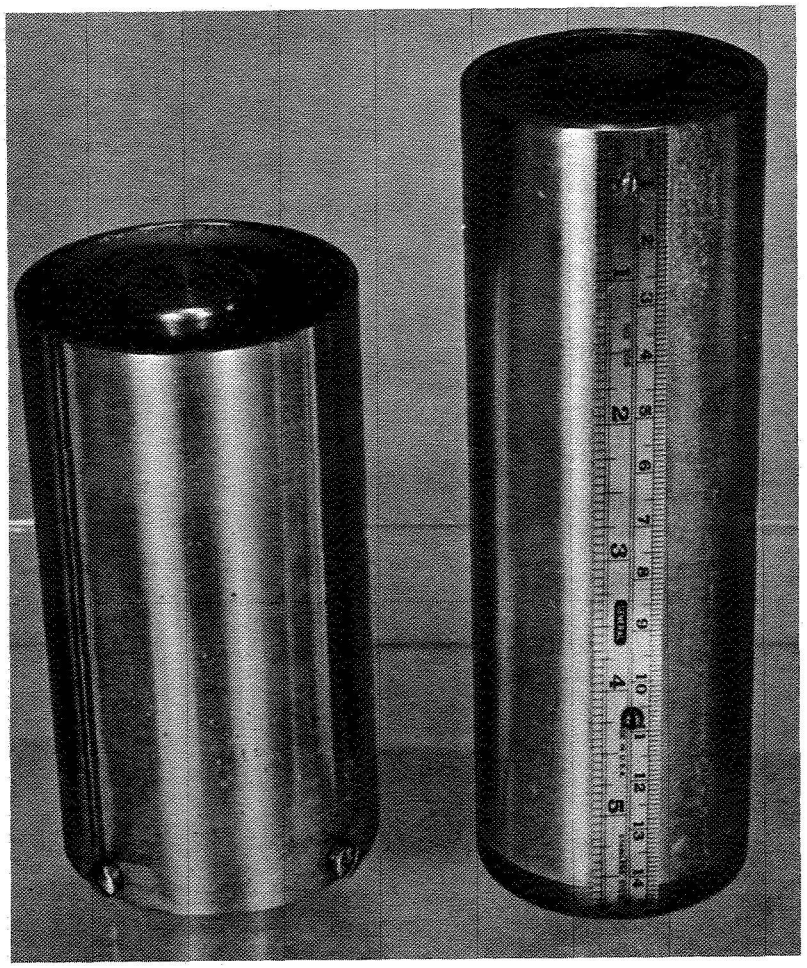
The conductivity or specific conductance (σ) is the electrical property which we calculated as a measure of the electronic properties of the mix.

$$\sigma = \frac{\ell}{A\Omega} = ohm^{-1}\ cm^{-1}$$

ℓ = height of test sample (cm)
A = area of test sample (cm^2)
Ω = resistance of test sample (ohms)

The area (A) is a constant (5.06 cm^2) which is characteristic of the ram in our apparatus. The height (ℓ) of the sample is measured. The resistance (Ω) is calculated from the voltage produced by an impressed current of 100 milliamperes. The use of conductivity ($ohm^{-1}\ cm^{-1}$) allows the comparison of data among samples of different sizes.

Data are taken both under pressure, and after the pressure was released.



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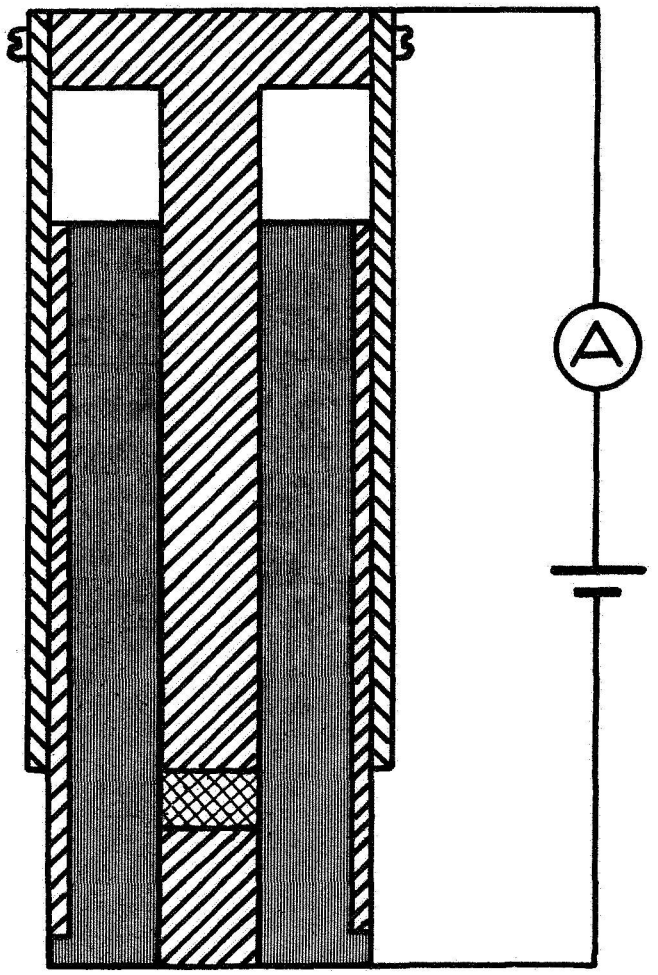


Schematic Cross Section

Figure 16. Cathode Mix Conductivity Cell.

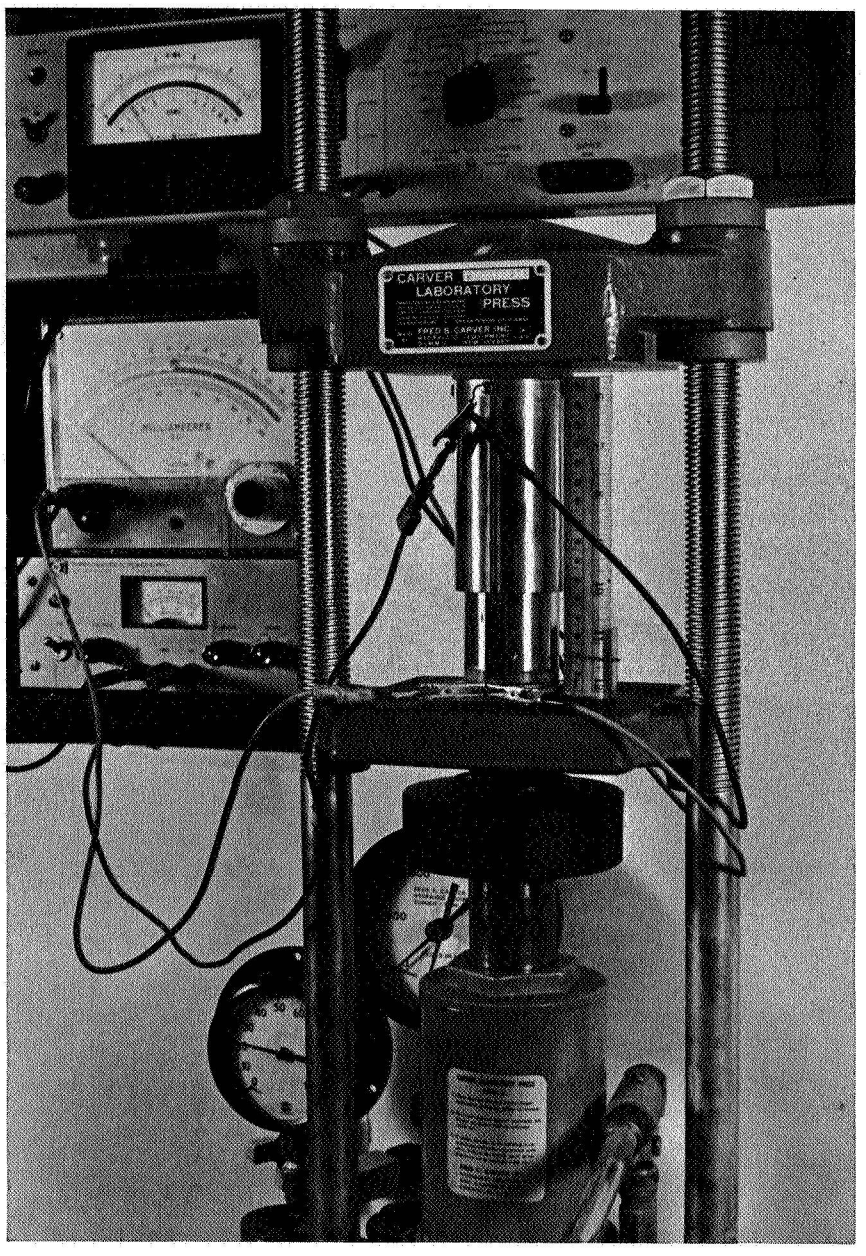


Figure 17. Conductivity Cell and Testing Apparatus.

Prior to the study of blending technique on mix conductivity, the conductivities of SAB and a standard cathode mix were determined.

Pressure-conductivity data for SAB is shown in Figure 18. While the conductivity of SAB under pressure increases in a regular manner with applied pressure, the conductivity of the material after pressure release remains relatively constant up to 2000 lb/in^2. Data at pressures higher than this tended to be unreliable. This unreliability is quite general (Appendix Tables A-1, A-2 and A-3) and is due to the formation of thin cracks in the test sample (parallel to its diameter) upon release of the pressure.

The addition of 6.5% carbon fibers causes little change in either the conductivity or density of SAB (105084 vs. 105083).

A number of basic data relating to pressure-conductivity relationships were generated using our standard cathode mix [83.4% DCA-70, 15.5% SAB, 1.1% carbon fibers (CF]. The cathode mix used in these initial measurements was the mix which was determined to be best from earlier empirical tests (ref. 1).

It was verified that data could be compared among samples of different sizes (105061a, 63, 83). The ability to utilize small test samples (e.g., 2.0 grams) was of interest because of possible safety considerations.

It was determined that the data obtained from two, standard 1.8 gram samples Waring blended for 0.5 min. each and combined, was the same as that from blending one 3.0 gram sample for 0.5 minute (105075, 76).

Neither the conductivity nor the density of the cathode mix is much changed by the elimination of the 1.1% CF component (105074, 81, 82).

The conductivity of our standard cathode mix as a function of applied pressure is shown in Figure 19. It can be seen that the sample conductivity under pressure is quite different from that of the pressure released sample (105081). The erratic behavior of the conductivity at pressures >2000 lb/in.^{2} is again noted (Table 13). These data indicate that cathodes pressed at >2000 lb/in.^{2} could have battery characteristics which are different from those prepared at lower pressures. Our cathodes are normally pressed at 300 lb/in.^{2}.

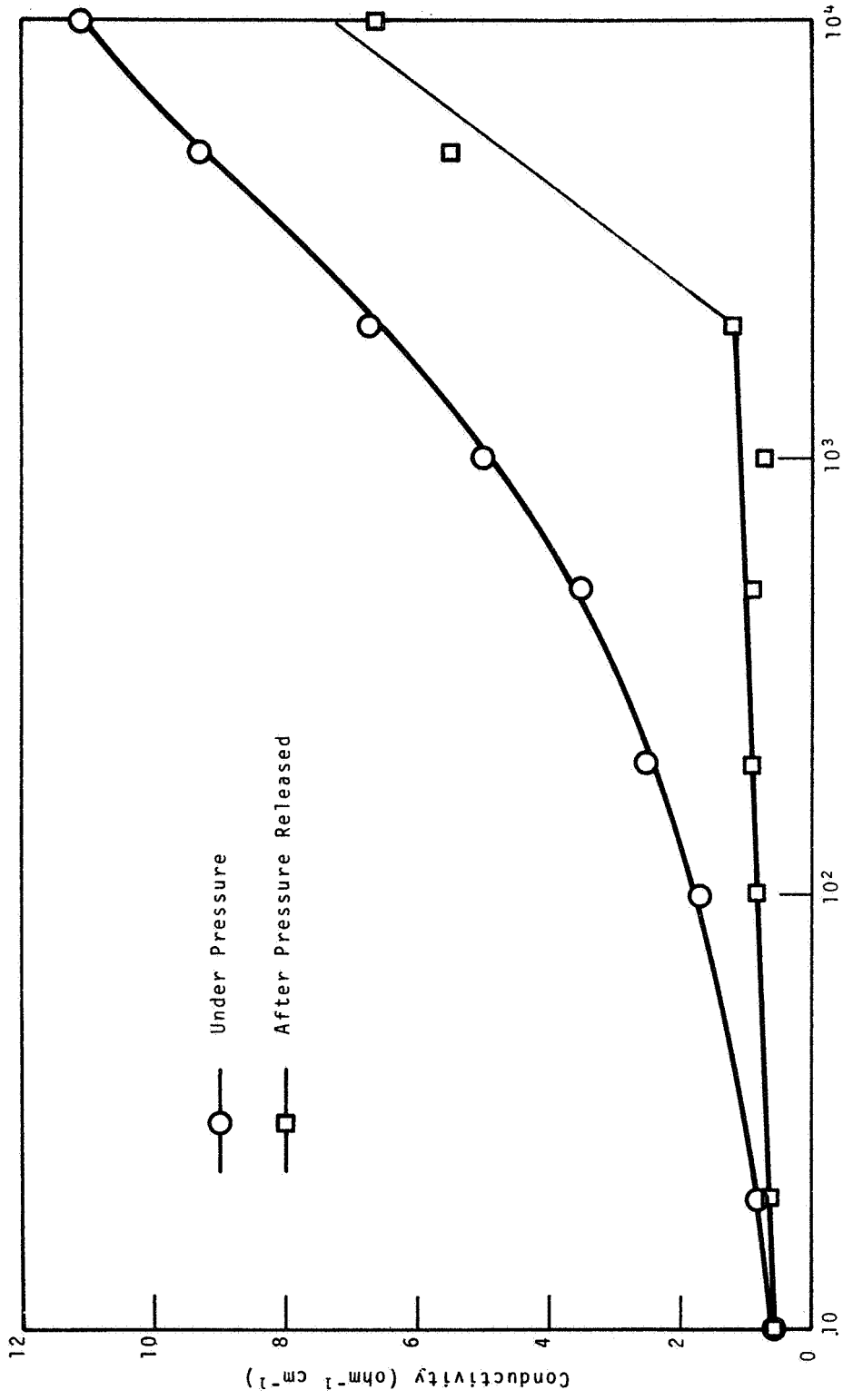


Figure 18. Electronic Conductivity of Shawinigan Acetylene Black as a Function of Applied Pressure.(105083)

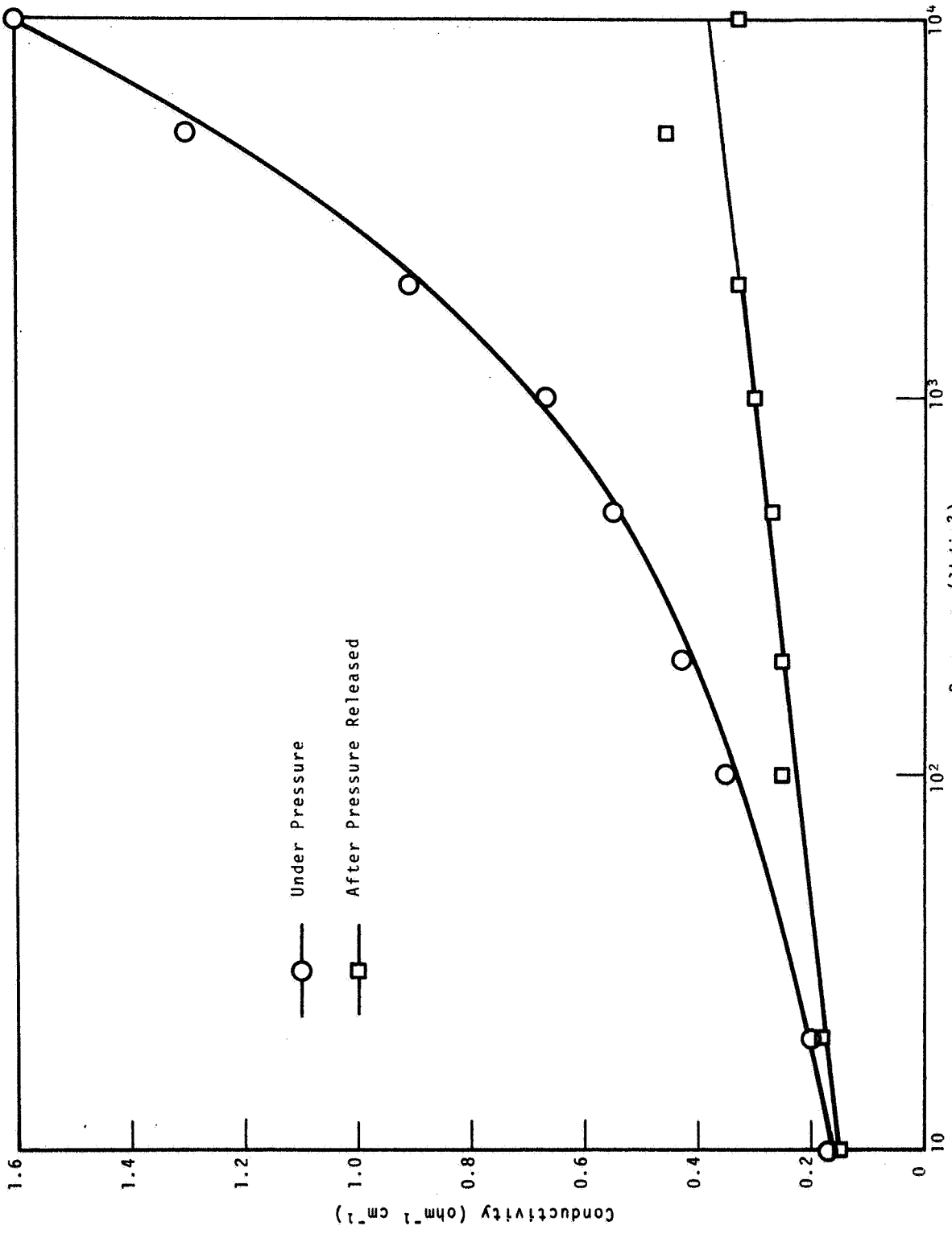


Figure 19. Cathode Electronic Conductivity as a Function of Applied Pressure for a Standard (Sample 105081) Cathode Mix

Table 13

RELATIONSHIP OF CATHODE MIX CONDUCTIVITY TO THE AMOUNT OF SAB IN THE MIX (105081) (15.5% SAB IN MIX)

Applied Pressure (lb/in^2)	Percent of Pure SAB Conductivity (Under Pressure)	Percent of Pure SAB Conductivity (Pressure Released)
10	30	30
20	29	28
100	23	28
200	20	30
500	17	29
1,000	13	42
2,000	13	28
5,000	14	8
10,000	14	6

e. General Density Data

The densities of SAB and our standard cathode mix are shown in Figures 20 and 21. The elimination of carbon fibers does not appreciably alter our cathode mix density.

f. Effect of Blending Technique on Mix Conductivity

The bulk conductivity of a battery mix is an important parameter, and a good indicator of blending effectiveness. Cathode mix conductivity is required for current transfer from the reaction site to the current collector plate. High bulk conductivity and uniform blending are both important for effective conduction of current from the reaction site.

Battery carbon blacks can be overmixed and the chainlike carbon structure broken. When this happens, the carbon conductivity drops sharply. This condition is especially prevalent when shear mixers, such as ball mills, are used.

As described above, the different mixes were screened by measurement of the conductivities at different pressures. The large number of experiments performed on this study are fully described in Appendix Tables A-1, A-2 and A-3.

The carbon (Shawinigan acetylene black and carbon fibers) was premixed in a Waring blender for one minute to break the carbon fiber (CF) agglomerates and to mix the CF with the Shawinigan acetylene black (SAB). The carbon fiber content was held at 1.1% of the entire mix in almost all cases. Three carbon percentages, 10, 17 and 24, were studied. The different ratios were mixed for various time periods, in three different blenders (Waring, Patterson-Kelly Twin Shell, and ball mill).

The conductivities and densities of different mixes were obtained. These data are given in Table A-2.

The most striking data obtained from the blending study are the high densities and low conductivities of samples ball milled for 1 hour or longer. These properties are undoubtedly due to attrition of the carbon structure. Densities and conductivities of 17% carbon samples after compaction at 200 psi are given in Table 14.

For each blending method, the conductivity is highest and density lowest for the sample blended for the shortest time. With the Waring or Patterson-Kelly (P-K) blender, the conductivity and density values remain relatively constant after a short mixing time.

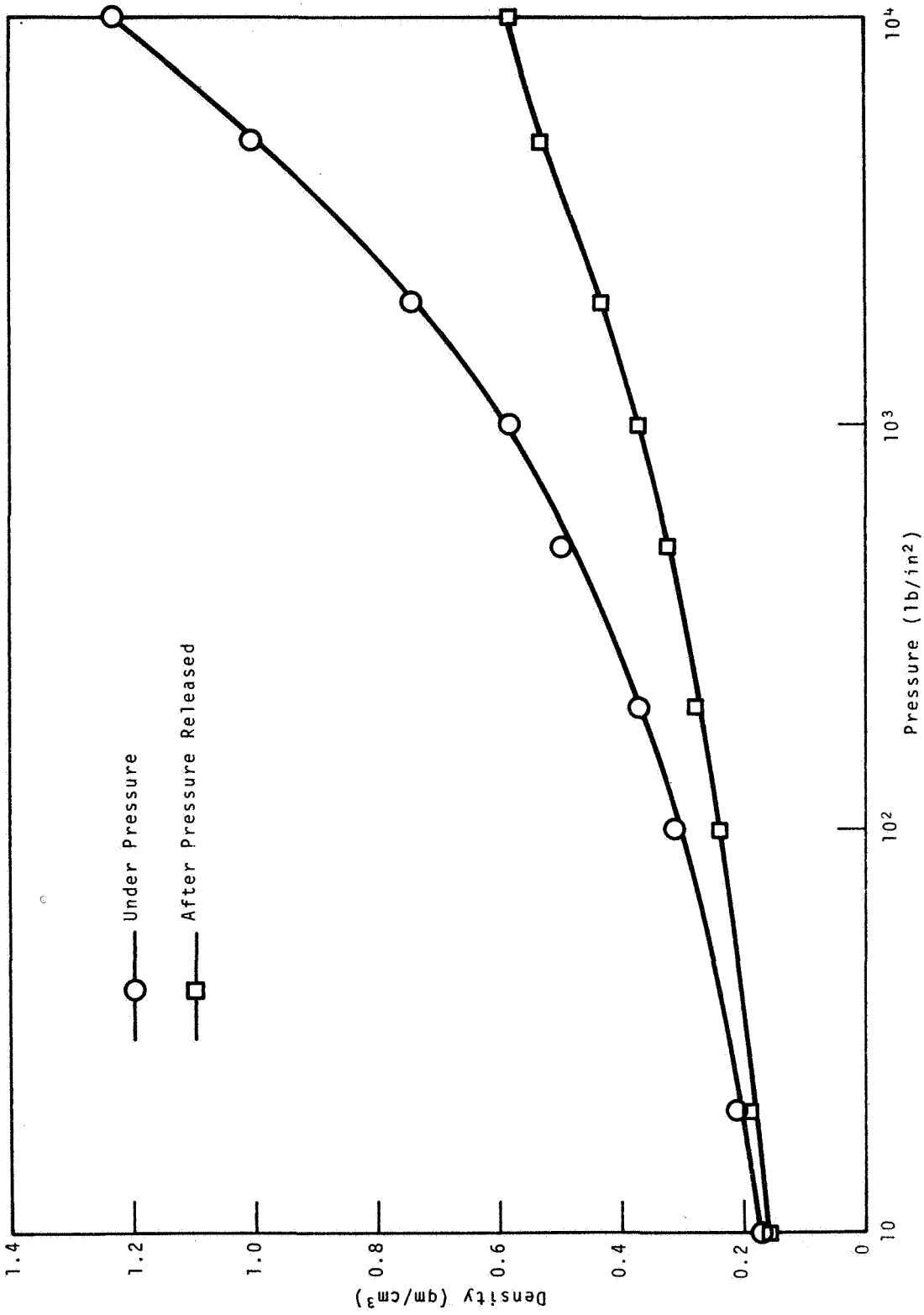


Figure 20. Density of Shawinigan Acetylene Black as a Function of Applied Pressure (105083)

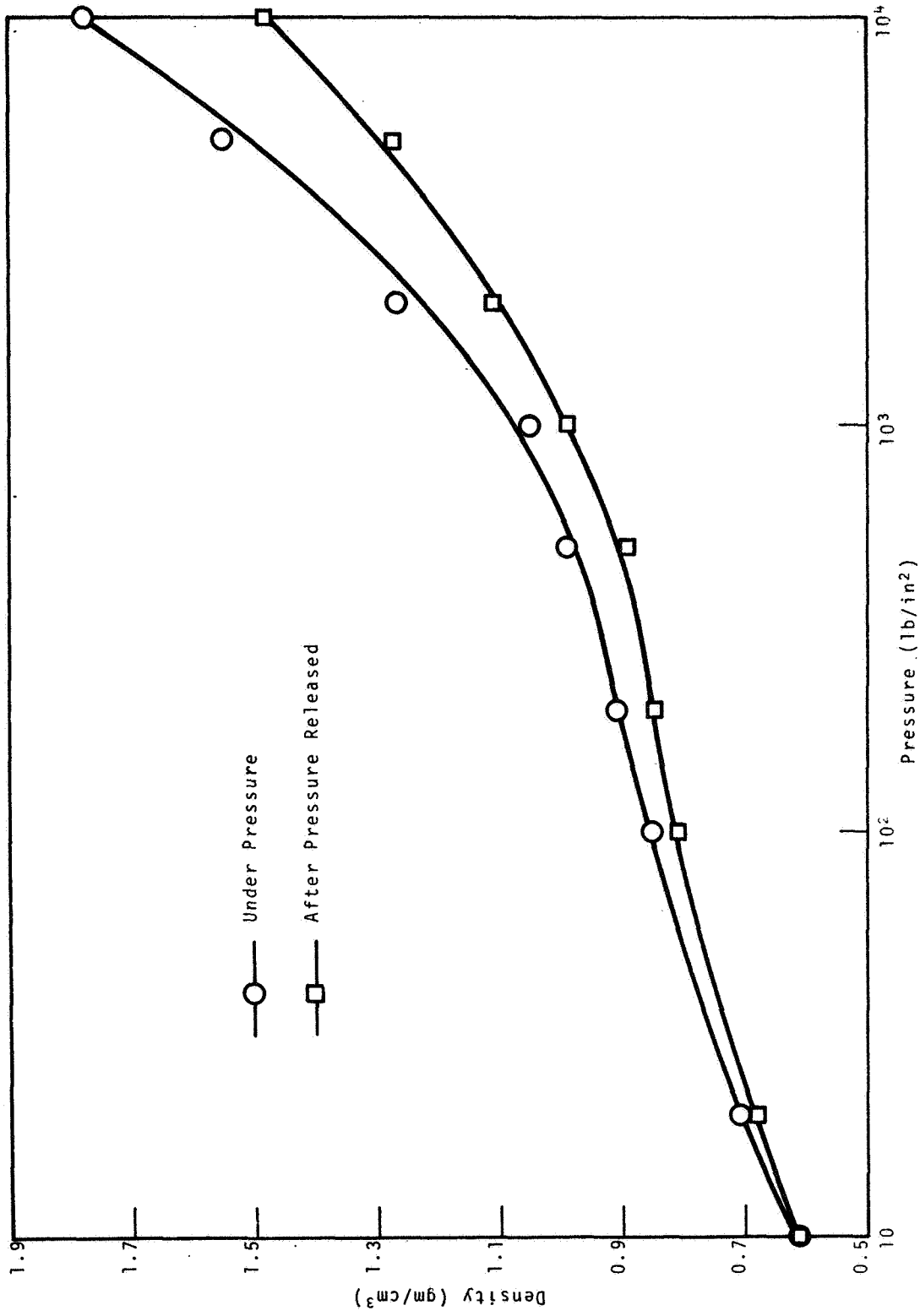


Figure 21. Cathode Density as a Function of Pressure for a Standard (Sample 105081) Cathode Mix

Table 14

EFFECT OF BLENDING ON MIX CONDUCTIVITY AND DENSITY
(17% CARBON, 200 PSI RELEASED)

Sample Type	Blending Time	Conductivity (ohm^{-1} cm^{-1})	Density (g/cm^3)
WB	0.5 min	0.240	0.82
WB	1.0 min	0.129	0.92
WB	2.0 min	0.157	0.93
WB	5.0 min	0.141	0.99
WB	10.0 min	0.099	0.99
PK	10 min	0.331	0.79
PK	1 hour	0.168	0.82
PK	8 hours	0.153	0.84
PK	24 hours	0.135	0.81
BM	10 min	0.076	0.86
BM	1 hour	0.066	0.97
BM	8 hours	0.0021	0.92
BM	24 hours	<0.0005	~1.01

Data reproducibility among Waring blended samples was good up to pressures of 2000 psi (Table A-1; 105074, 82; 1050616, 63, 83; 105061a, 83). The ball milled samples showed comparatively poor reproducibility (Table A-2; 105091, 82865, 105097 a, b, 82857, 82865), even within one batch of mix. Reproducibility between batches is approximately the same. Gross inhomogeneities were found in the ball milled samples. The one hour P-K blend samples showed good reproducibility within a given batch (Samples 109201 a, b, 109203).

Data were also collected on DCA-70 decomposition as a function of blending and pressing. The results are shown in Table 15 and indicate significant decomposition only for samples ball milled for more than one hour.

Table 15

EFFECT OF BLENDING AND PRESSING ON DCA-70 STABILITY

Blending Method - Time		% Decomposition After Blending	After Pressing (2000 psi)
WB	1.0 min.	0	1
WB	2.0 min.	0	1
WB	10.0 min.	1	5
PK	1 hour	0	NM
PK	24 hours	1	NM
BM	1 hour	0	NM
BM	24 hours	7	NM

NM = not measured

Representative data are shown in Table 16 for the 1 hour PK blend, compressed to 200 psi and the pressure released, for various carbon contents. Complete conductivity-density data are given in Appendix Table A-2.

Table 16

DENSITY AND CONDUCTIVITY DATA AS A FUNCTION OF CATHODE CARBON CONTENT (1 HR P-K, COMPRESSED TO 200 PSI AND RELEASED)

Sample	% Carbon	Density	Conductivity (ohm^{-1} cm^{-1})
82862	10	0.942	0.087
109201a	17	0.824	0.168
82863	24	0.698	0.369

The absolute densities of SAB and DCA-70 are 1.95 and 1.78 g/cm^3, respectively. Hence, it is evident that the void volume rises rapidly with increasing carbon content. As expected, the conductivity (ohm^{-1} cm^{-1}) of the mix also rises with increased carbon content.

g. Effect of Blending Technique on Cell Discharge Characteristics

(1) Effect of Blending

The general conclusion drawn from our data is that the least blending produces the best cathodes (Table 17). At 1 hour of ball milling, the performance is bad due to overmixing and attrition of carbon black structure. In general, there is a good correlation of energy output with conductivity. However, visual observation of the mixes indicates that after only 10 min. in the P-K Twin Shell blender, the DCA-70 is not well blended with the carbon. White particles, or agglomerates, of DCA-70 are readily visible throughout the mix. Complete data are given in Appendix Tables A-4 and A-5.

(2) Effect of Carbon Pre-Mixing

When the 50% compressed Shawinigan acetylene black (SAB) was used without pre-fluffing in the Waring Blender, a very poor mix was obtained even after 20 minutes in the P-K blender. Hence, a 1 minute pre-mixing of SAB and carbon fibers (CF) was used for the blending studies. This relatively drastic treatment was needed to disperse the CF in the SAB. Elimination of the CF was necessary in order to reduce or change this pre-mixing. The data, shown in Table 18, indicates that the CF is not critical to the test cathodes.

Three pre-fluffing or de-agglomeration methods were tested. The tests were cell discharges of 10 min. P-K blended material. The methods were (1) the standard 1 min. WB pre-fluffing, (2) screening of 50% compressed SAB through a 50 mesh sieve, and (3) uncompressed SAB, used as received. Summary data are shown in Table 19.

The most unusual mix was obtained with the screened carbon. This mix was not readily compressible and required 1.7 ml of electrolyte (1.5 ml is normal) to achieve even a moderate wetness. However, the visual appearance of these blends after 10 min. P-K blending was identical.

Table 17

EFFECT OF BLENDING ON DISCHARGE
(17% Carbon, 10 mA/cm^2, 0.05", 20 cm^2)

Cell No.	Blending Method-Time	Average Volt(v)	Efficiency (%)	Energy Density (w-hr/lb)
109316	WB - 0.5min	3.15	58.1	169
109314	WB - 0.5min	2.77	52.1	133
109313	WB - 2.0min	2.76	49.6	126
109312	PK -10 min	2.99	54.8	151
109309	PK - 1 hr	3.06	51.2	145
109311	PK - 8 hr	3.02	47.7	136
109331	BM -10 min	3.07	55.0	160
109310	BM - 1 hr	3.01	38.5	107

Table 18

EFFECT OF CF ELIMINATION ON DISCHARGE
(17% Carbon, 1 min WB pre-mix, 10 mA/cm^2, 0.05", 20 cm^2)

Cell No.	CF	Blending Method-Time	Average Volt(V)	Efficiency (%)	Energy Density (w-hr/lb)
109316	yes	WB - 0.5min	3.15	58.1	169
109315	no	WB - 0.5min	3.15	57.0	166

Table 19

EFFECT OF CARBON PRE-MIX ON DISCHARGE
(17% Carbon, 10 min P-K, 10 mA/cm^2, 0.05", 20 cm^2)

Cell No.	Pre-Mix	Average Volt(V)	Efficiency (%)	Energy Density (w-hr/lb)
109317	1min WB	3.18	57.9	170
109318	Uncompressed	3.14	54.5	158
109320	Screened[1]	3.19	59.9	166

[1] Used 1.7 ml electrolyte instead of 1.5 ml

Several additional experiments were carried out on carbon de-agglomerization by mesh screening (Table 20). Larger quantities of electrolyte were required to give adequate performance with de-agglomerated SAB. There was no evidence that screening the carbon black improved performance.

Table 20

EFFECT OF CARBON PRE-MIX ON CELL DISCHARGE
(10 min P-K, 10 mA/cm^2)

Cell	Pre-Mix Screening (mesh)	Electrolyte Volume(ml)	Average Voltage(V)	Efficiency (%)	Energy Density (w-hr/lb)
109320	50	1.7	3.19	59.9	166
109330	50	1.8	3.17	56.3	151
109250	20	1.7	3.12	55.0	149

(3) Effect of Blending Time

While less blending was found to improve cathode discharges, there was no mixing technique proven better than the Waring method. For this reason, tests were run using this blender for periods shorter than our conventional times of 30 seconds. Results are given in Table 21. The data indicates a slight advantage for blending only 10 seconds.

4. Effect of Binders on Cathode Structure

a. Preparation of Samples

Three binders were chosen for evaluation. These were Teflon (TFE), polyvinylchloride (PVC) and Kynar (vinylidine fluoride). Each was a dry free-flowing powder. None would react with DCA-70, nor dissolve in the $LiClO_4$-MF electrolyte. Each binder was added in 1, 3, 5, or 10% concentration, and dry mixed with the cathode materials by Waring blending for 30 seconds.

Samples were pressed in the standard apparatus for determining conductivity and density. Tapes of 1" x 3" dimensions were prepared for testing structural integrity.

An attempt was made to prepare a Teflon dispersion using various non-reactive solvents. A rather unstable 0.1% TFE dispersion was prepared in chloroform using a Waring blender. Before the TFE settled out, the carbon and DCA-70 were added and mixed in the Waring blender. The cathode was pressed into the 1" x 3" die before drying and tested for integrity after drying.

Table 21

EFFECT OF TIME OF WARING BLENDING ON CELL DISCHARGE
[10 mA/cm^2, 1.5 ml, 2.0M $LiClO_4$(MF)]

Cell	Blending Time(sec)	Average Voltage(V)	Efficiency (%)	Energy Density (w-hr/lb)
109313	120	2.76	49.6	126
109332	30	3.17	55.4	162
109333	30	3.22	52.6	156
109334	30	3.20	52.9	156
109335	30	3.08	58.5	164
109246	10	3.18	58.6	172
109340**	5	3.05	56.1	149
109338***	5	3.18	56.7	166

** Required 1.7 ml electrolyte
*** Carbon pre-blended for 10 seconds. Normal is 60 seconds in Waring blender before 30 second mix blending.

b. Conductivity-Density Data

Conductivities for mixes of dry binder powders and cathode materials are presented in Table A-3 and summarized in Table 22.

The effect of 1-3% binder is small in all cases. At 10% binder, the conductivity of the mixes containing Teflon and PVC is lowered considerably.

c. Strength of Tapes

Tapes were prepared by blending dry ingredients for 30 seconds in the Waring blender. These tapes of 0, 5 and 10% TFE, were pressed at 300 psi for 2 minutes. Thus, the 0% TFE tape is a standard tape for discharge. Each tape (1" x 3") was placed on a 1/2" rod, and each broke before bending more than $\sim 30°$. The 10% TFE tape was somewhat stronger.

Table 22

CONDUCTIVITIES OF MIXES CONTAINING BINDERS
(0.5 min.WB, 17% Carbon, Pressure 200 psi)

Cell No.	Binder	Density (g/cm^3) N *	Conductivity (ohm^{-1} cm^{-1}) P**	N*
105076	None	0.82	0.42	0.24
109208	1% TFE	0.83	0.36	0.25
109209	3% TFE	0.80	0.39	0.28
109218	5% TFE	0.86	0.28	0.08
109219	10% TFE	0.87	0.21	0.04
109210	1% Kynar	0.81	0.41	0.33
109210	3% Kynar	0.81	0.38	0.25
109229	10% Kynar	0.82	0.32	0.18
109220	1% PVC	0.84	0.28	0.17
109220	3% PVC	0.82	0.36	0.20
109320	10% PVC	0.88	0.14	0.06

* N = After release of 200 psi

** P = 200 psi applied

The tapes prepared for an earlier contract (ref. 1), were pressed out from a slurry. Therefore, a tape was prepared with 10% TFE using chloroform as the slurry agent. This tape also had poor mechanical properties.

The use of a roughened (pilled) separator and longer carbon fibers might increase tape strength without the use of binders. A binder which is soluble in a solvent that does not react with DCA-70, and which is insoluble in methyl formate would also be advantageous.

5. Cathode Photomicrography

a. Introduction

A direct method for studying the effect of blending technique on cathode physical properties is microscopic examination. The dispersion of carbon has been studied in the rubber industry by photomicroscopy (refs. 22, 23). Similar methods were applied in this program. Thin cathode layers are required for this purpose. While a microtome might be used to section thin layers, the cathodes were very brittle and needed a binder phase to hold it together during sample preparation.

b. Sample Preparation

Several binder phase materials were studied. Several epoxy resins were first tried. The amine curing agents reacted with DCA-70, however,

A successful method was developed, using wax vacuum impregnation. To avoid break-up of the fragile cathode, a vacuum was pulled on the system before the sample was immersed into molten wax. The wax impregnation device is shown in Figure 22. The resulting sample was sectioned with a microtome at room temperature. The sections were then suspended on a non-reactive, immiscible liquid, such as Freon TF, for microscope slide preparation.

The wax impregnated cathodes were sectioned on a Reichert sledge microtome.

c. Microscopic Examination

Optical photographs were taken with a Polaroid camera mounted on an American Optical binocular microscope. Electron micrographs were obtained with a JEOLCO electron microscope. Figure 23 shows sections of a standard cathode cut to 2 and 5 micron thicknesses. Since the magnification in the photograph is 120X, each millimeter equals 8.5 microns.

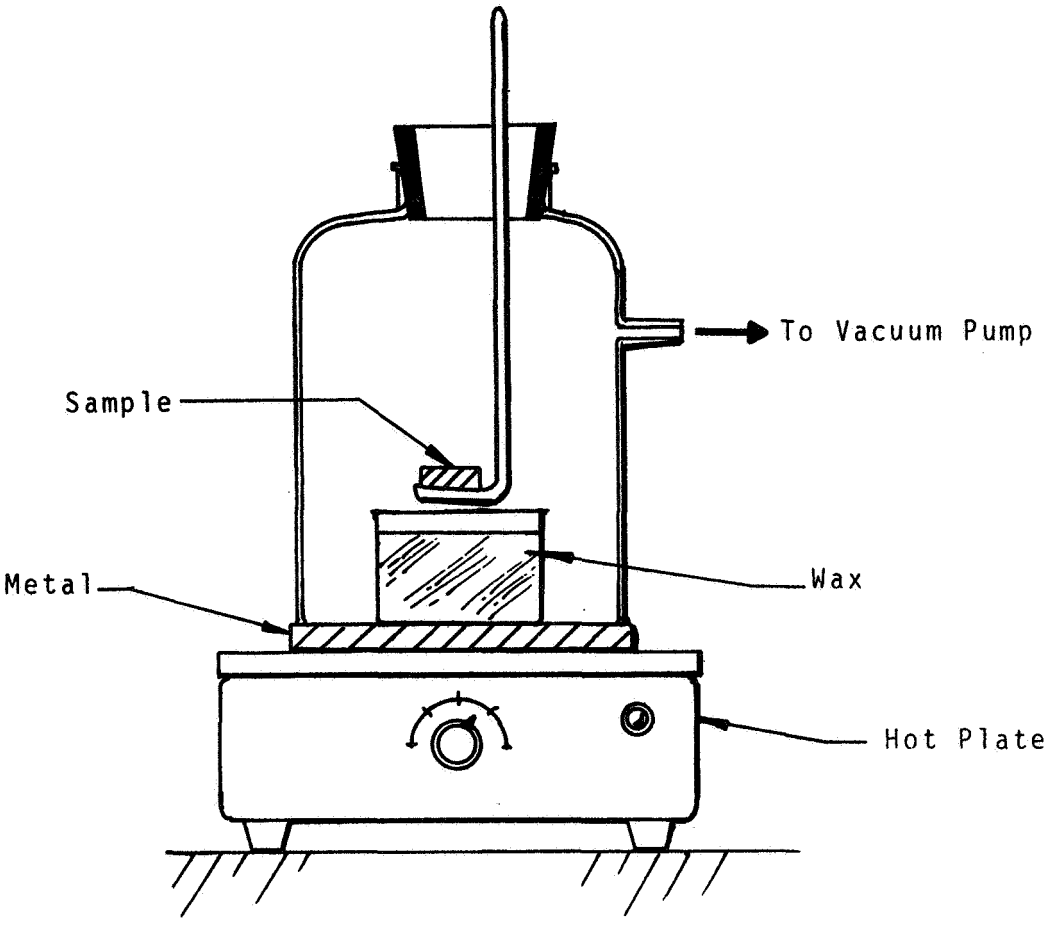
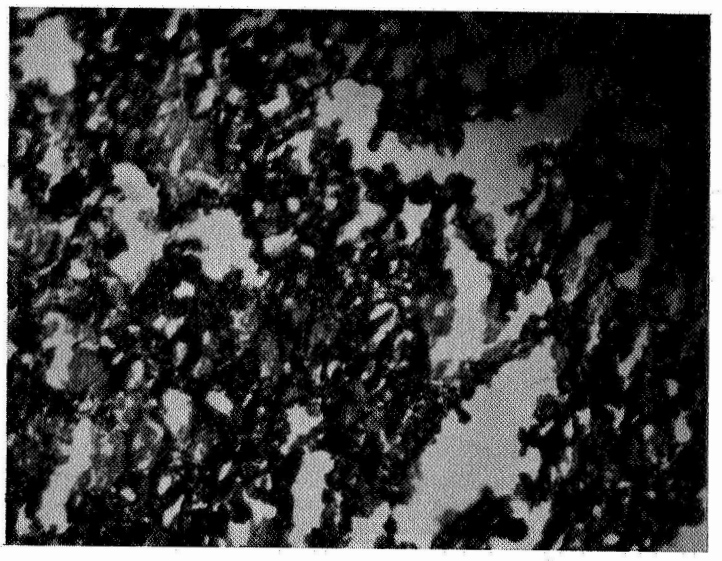
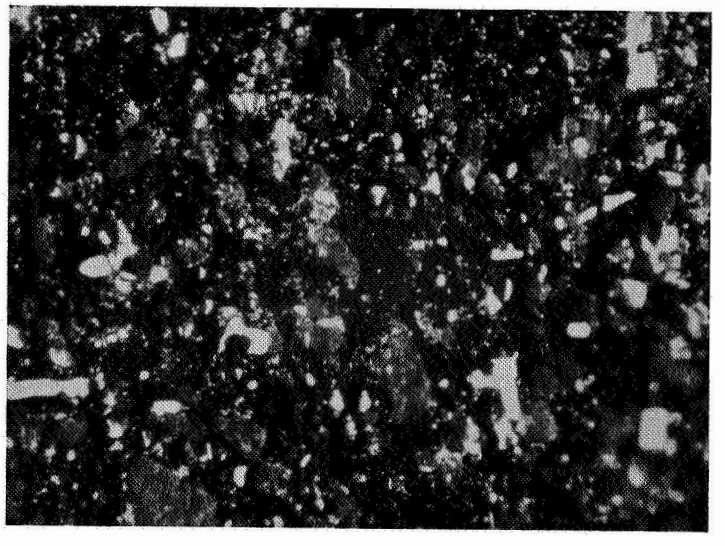


Figure 22. Schematic of Wax Impregnation Device



2μ Section (X120)



5μ Section (X120)

Figure 23. Optical Photomicrographs of Microtomed Cathode.

The black areas in these photomicrographs are carbon, and the white areas are voids. The gray areas are presumably DCA-70. Since both wax and DCA-70 crystalline, it is difficult to obtain information with the petrographic microscope technique (crossed Nicols). From the 2μ section, it appears that the DCA-70 is coated with carbon chains. The carbon fibers may also aid the chain formation. In the 5μ section, the DCA-70 particles stand out as gray areas and their distribution can be determined.

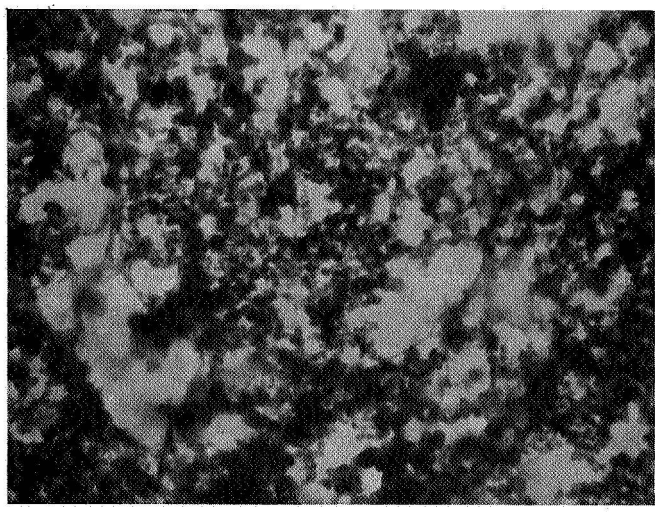
Figures 24 and 25 show electron micrographs taken of cathode mix samples supported in both epoxy and wax. The epoxy sample was microtomed in 800-1000 A sections and observed directly. A replica technique was employed for the wax samples. In these pictures the primary carbon particles (∿450 A) can be seen, and the effect of mixing on chain structure could presumably be determined as a function of mixing method. Identification of DCA-70 in these micrographs is not certain.

Optical photomicrographs were obtained on surfaces and transverse cuts of discharged cathodes. Figure 26 shows the effect of discharge on the separator and collector surfaces (magnification 7X). The more complete the discharge, the more large white crystals are evident. This is especially true of the collector surface. Binocular observation, however, indicates that these crystals cover the sides of cavities in the cathode and are not necessarily on the collector surface. The cathodes in Figure 26a and 26b were disconnected at 1.0 volt and separated from the anode at that time. Figure 26c shows the surface after discharge to 3.0 volts (ca. 2/3 discharged). Figure 26d is the surface of the cathode without discharge and both surfaces are identical.

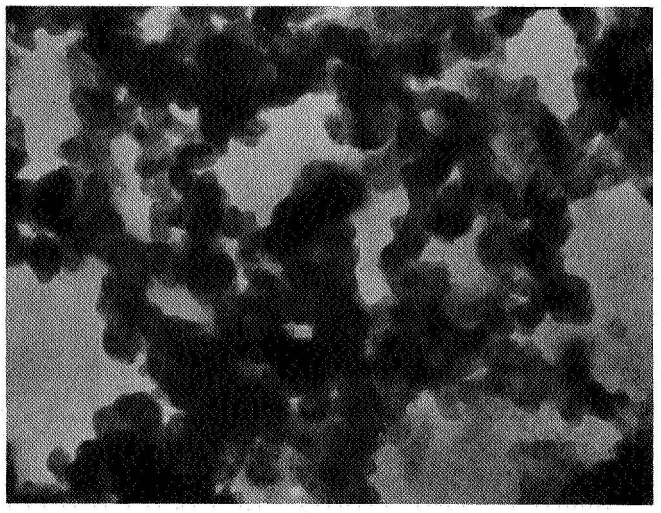
These same samples were sectioned perpendicular to the surface using a sledge microtome. The wax impregnated 10μ sections were photographed at 130X. Some of the sections are shown in Figure 27. No large crystal segregation was noted at either edge of the discharged section. Also, no obvious difference can be seen between the discharged and undischarged cathode. It was noted that most cathode structure was parallel to the surface. Thus, carbon fibers, fissures, and large DCA-70 agglomerates were oriented with their major axis parallel to the surface.

The total cross section of an undischarged cathode is shown in Figure 28. The gray DCA-70 appears to be well dispersed among the black SAB and white voids.

X15,000



X15,000



X30,000

Figure 24. Electron Micrographs of Wax-Impregnated Cathode Mix (Replica Technique)

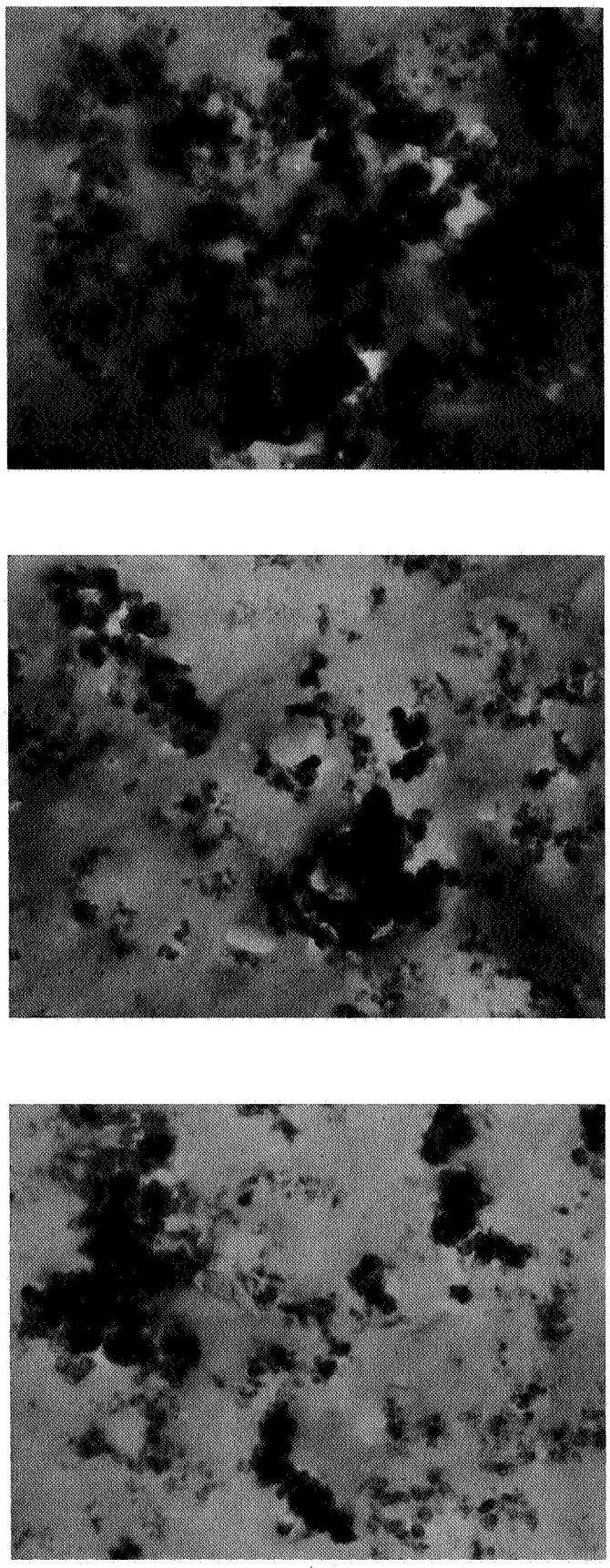
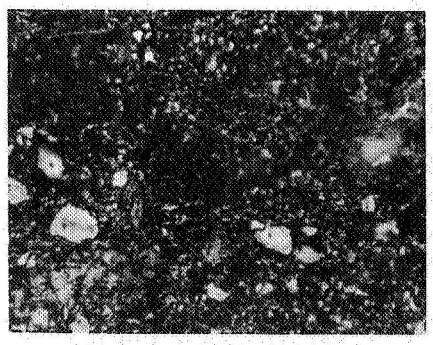
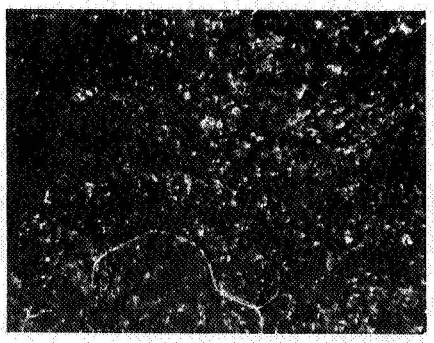


Figure 25. Electron Micrographs of Epoxy-Impregnated Cathode Mix (0.1μ Sections, X15,000)



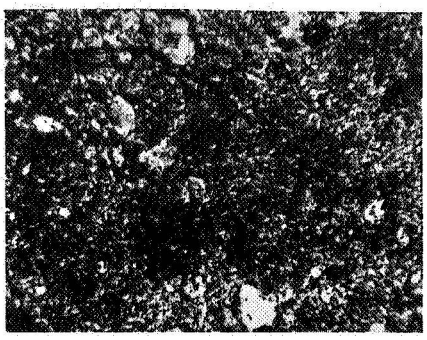
Collector Side



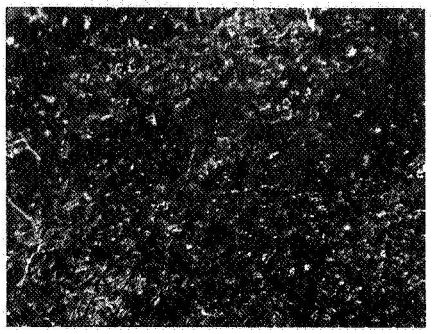
Separator Side

Discharged Cathode 109251-to 1.0 volts

26a



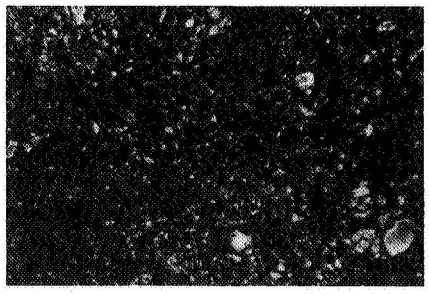
Collector Side



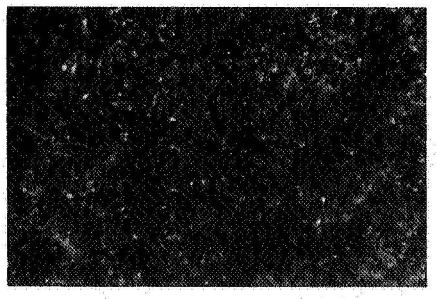
Separator Side

Discharged Cathode 109253-to 1.0 volts

26b



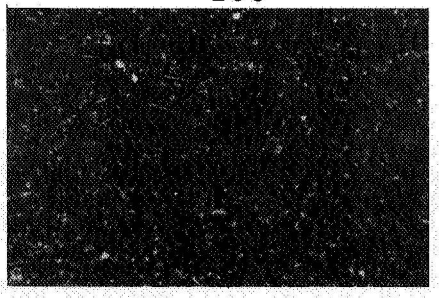
Collector Side



Separator Side

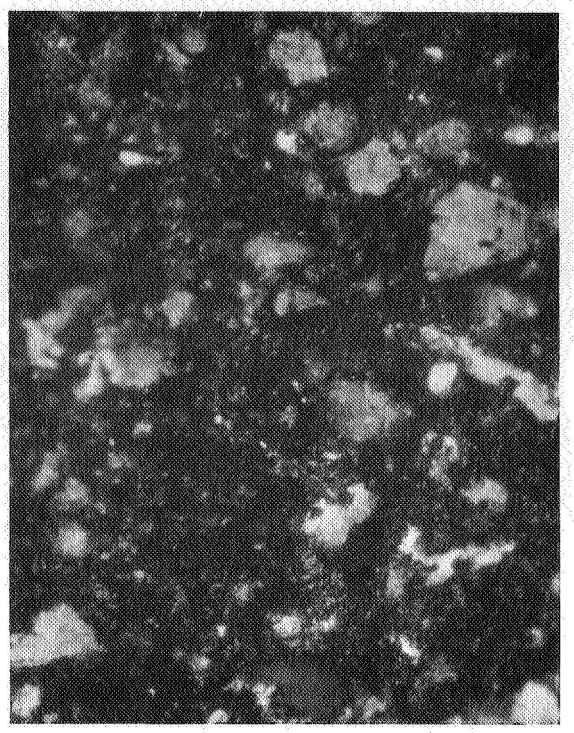
Partially Discharged Cathode-to 3.0 volts

26c



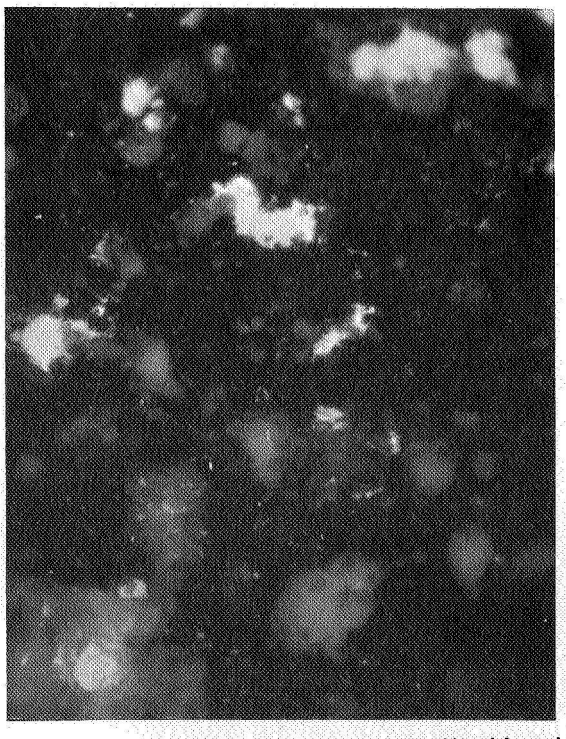
Undischarged Cathode

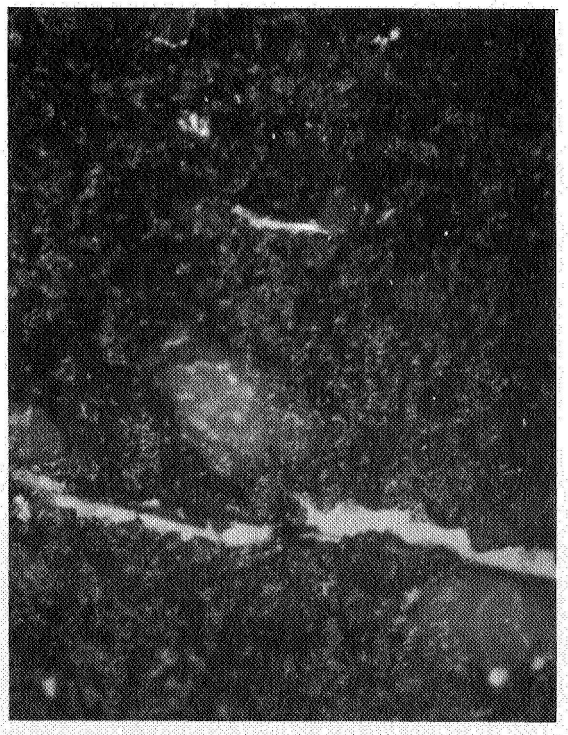
Figure 26. Photomicrographs of Cathode Surfaces - 1 hour, P-K Blend. (15X)



Totally Discharged Cathode
109253

Partially Discharged Cathode
to 3.0 volts





Undischarged Cathode

Figure 27. Photomicrographs of Cathode Cross-Sections 130X

Figure 28. Total Cross-Section of an Undischarged Cathode (130 X)

C. VOLTAMMETRIC STUDIES OF DCA-70 and TCA-85

1. Coulometric Studies

a. DCA-70

(1) Platinum Electrode Studies

A rotating electrode study of DCA-70 solutions could provide basic information for the evaluation of the limiting factors in our DCA-70 cathodes. Important to this study, however, is a prior knowledge of the reduction products of DCA-70. Coulometric studies were carried out on DCA-70/$LiClO_4$-MF solutions with a Pt electrode in order to obtain this necessary data.

An unexpected problem developed when it was discovered that a white precipitate formed on the Pt electrode during discharge. This occurred over a 50 fold DCA-70 concentration range (Table 23). Even with efficient stirring, the precipitate from the 1% solution blocked the electrode after 20 coulombs (9% efficiency) had been passed. When the precipitate ($\sim$1.5 mg/cm^2) was scraped off the electrode, it was found to contain between 10% and 35% chloride ion, but no active chlorine. An infrared spectrum of the solid (KBr pellet) showed the presence of an organic compound, with a spectrum similar to, but not identical with, cyanuric acid (Fig. 14).

Coulometric experiments at low concentrations of DCA-70 were conducted to verify that the electrode reaction was simple, and that it was a four electron transfer reaction (Table 23). In these experiments, however, unusual voltage-time curves were obtained. This behavior is presumably due to precipitation on the electrode, which does not occur in the high rate chronopotentiometric experiments discussed in the following section. A voltage increase is observed (Figure 29) which might be explained as follows:

> Product crystals form, and further reaction is aided by further product crystallizing readily into the already formed lattice. Voltage increases from this effect have been observed in the Ag/AgCl system (ref. 7).
>
> After the voltage maximum, some voltage oscillations occur, presumably due to buildup and then breakage of a tight film on the electrode.

Table 23

COULOMETRIC EXPERIMENTS WITH DCA-70
(2M $LiClO_4$-MF, 12 ml Solution Volume, Pt Electrode)

Cell No.	Concentration DCA-70 (moles/ℓ)	Current Density (mA/cm^2)	Reduction Efficiency (%)
105026b	0.050	5.0	9.1
105027	0.050	5.0	9.3
105035	0.050	5.0	7.5
105026c	0.050 + Products*	5.0	2.0
105030b	0.050	2.5	12.0
105030a	0.025	2.5	23.0
105032	0.005	0.5	26.5
105033	0.005**	0.5	31.7
105034	0.001**	0.1	34.0

* Products in solution from Test 105026 - clean electrode used.

** Pure MF from 4A molecular sieve procedure.

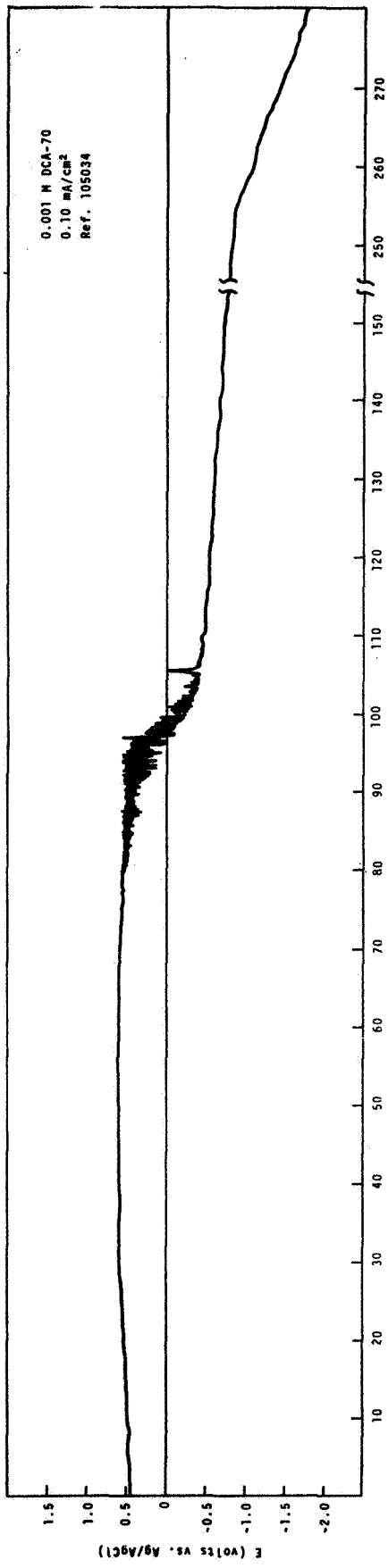


Figure 29. Coulometric Voltage-Time Plot

Finally, the voltage reaches a lower plateau, which is due to the overpotential from slow diffusion or slow ion migration through the porous layer of products. This plateau voltage may be due to resistance polarization, as shown in interruption experiments in our earlier work (ref. 1). The crystallization phenomenon may also explain the maxima in currents and voltages observed in full cell discharges.

(2) Carbon Electrode Studies

A carbon-epoxy electrode, with properties more similar to our cathode was tested using 0.001N DCA-70 at 0.10 mA/cm^2. A comparison was made with the results from a platinum electrode run (Figure 29). During this run, oscilloscope data concerning polarization relaxation was obtained. Thus, if the build-up of products on the electrode leads to IR polarization, this should be very evident in the oscillograms (the resistance polarization relaxes immediately). However, with the carbon electrode, the open circuit (as measured through 1 megohm) was only +0.8 volts vs. Ag/AgCl. Also, at 0.10 mA/cm^2, the electrode polarized immediately to -0.01 volts. The polarization increased to -0.60 volts at 280 minutes, and then slowly recovered. Hence, the accumulation of products was different at this electrode from the previous platinum test.

The carbon-epoxy electrode was also tested using 0.05M DCA-70 at 5.0 mA/cm^2. Under these conditions, the electrode again polarized immediately to $\sim$0.0 volts vs. Ag/AgCl, and then at 75 min. the potential fell quickly to $<$-2.0 volts, indicating precipitate coverage of the electrode. The electroproduced material is probably basically the same at the carbon and platinum electrodes.

A Dry Tape cathode, however, is not required to run under such stringent conditions. Our cathode contains 0.3 gram of carbon (surface area of 5×10^5 cm^2/g) which indicates a true current density of the order of 1μA/cm^2. Furthermore, the solution is saturated with DCA-70. For this reason, a long term test was made at 10μA/cm^2, using a saturated (0.75M) DCA-70 solution in 2M $LiClO_4$ (methyl formate). No stirring was used in this test. The test was run for 100 hours, which would consume 0.06 amp-min. of the 54.1 amp-min. of DCA-70 in solutions. After the test, 80% of the DCA-70 remained in solution. No precipitate was evident at the electrode after the run, and the voltage only dropped from +0.70 volts (initial) to +0.50 volts vs. Ag/AgCl after 100 hours. This suggests that the precipitate which forms in some of the half cell electroreductions may not be responsible for the limited cathode efficiencies in our Li/DCA-70 cell.

Since additional carbon in the cathode plate had been found to increase the cathode efficiency (see Section II.D), it was thought that the cathode limitation might be a precipitate which covered the active carbon surface. If this was true, then the efficiency could be improved by increasing the solubility of the product, or by making the precipitate more porous. Therefore, the following experiments were carried out.

A dense carbon rod was waxed on its sides and inserted in the test solution. The electrode face was sanded with fine emery paper after each test. The reduction was performed at constant current. The solution was not stirred and the potential was recorded versus a silver reference electrode. Sharp passivation potential steps were observed in all cases at time (τ). The data are shown in Table 24.

The amount of reduction before passivation ($i\tau$) decreases with increasing current density. The value of $i\tau^{1/2}$ is approximately constant. This is expected if the layer of precipitate is relatively porous. The potential break is due to the concentration of a reactant reaching zero at the electrode surface. By increasing the concentration of DCA-70 in the solution, the time to reach passivation increases moderately. This increase is less than that obtained in chronopotentiometry ($i\tau^{1/2} = kc$), and follows a $i\tau^{1/2} = kc^{1/2}$ relationship more closely. The chronopotentiometric form can be realized assuming the porous layer increases in thickness as follows:

$$i = nFAD\left(\frac{\Delta C}{l}\right)$$

$$i = nFAD\left(\frac{C}{ki\tau}\right)$$

$$\frac{i^2\tau}{C} = \frac{nFAD}{k}$$

In practice, the area of the electrode also changes, and the quantity of precipitate in the layer and its physical form is not uniform or a simple function of it. Hence, the passivation equation form is often expressed best as $i\tau^n = k$, where $1.0 < n > 0.5$. In the above data, $n < 0.5$ is observed.

The passivation time is not greatly affected by saturating the solution with LiCl. Hence, there is no direct evidence that LiCl precipitation is the principal passivation mechanism. The solubility of LiCl in $2M LiClO_4$(MF) is 6.7 g/l, and 1.1 g/l in pure solvent (MF).

Table 24

PASSIVATION STUDY OF DCA-70 REDUCTION ON CARBON

DCA-70 (M)	$LiClO_4$ (M)	Additive	Current Density i (ma/cm^2)	τ (min)	$i\tau$	$i\tau^{1/2}$
0.10	2.0	None	2.0	65	130	16
0.10	2.0	None	3.0	26	78	15
0.10	2.0	None	5.0	6.0	30	9
0.25	2.0	None	2.0	132	264	23
0.25	2.0	None	3.0	41	123	19
0.25	2.0	None	5.0	12	60	17
0.10	2.0	LiCl sat'd	2.0	81	162	18
0.10	2.0	LiCl sat'd	3.0	30	90	16
0.10	2.0	LiCl sat'd	5.0	7.5	38	14
0.25	2.0	LiCl sat'd	2.0	136	272	23
0.25	2.0	LiCl sat'd	3.0	30	90	16
0.25	2.0	LiCl sat'd	5.0	12	60	17
0.10	2.0	H_2O 1%	3.0	26	78	15
0.10	2.0	MeOH 1%	3.0	24	72	15
0.10	2.0	AN 1%	3.0	24	72	15
0.10	3.0	None	3.0	5.0	15	7
0.10	3.0	None	3.0	5.9	18	7
0.10	2.0	None	3.0	22	66	14
0.10	2.0	None	3.0	21	63	14
0.10	1.0	None	3.0	23	70	14

The addition of polar solvents (water, methanol or acetonitrile) could increase the solubility of salt products, such as LiCl as the lithium salts of cyanuric acid. However, addition of 1% (by volume) of these solvents did not change the passivation times.

A large effect was noted with a change in the concentration of $LiClO_4$. At high $LiClO_4$ concentration, passivation is rapid. Thus, high Li ion concentration apparently increases the speed of precipitation, giving a dense layer of high coulombic efficiency. At lower $LiClO_4$ concentration, (e.g., 1M), there is either no effect, or the lower amount of precipitation is offset by the lower conductivity of electrolyte in the porous layer.

The possibility of depletion of $LiClO_4$ in the precipitate layer due to the Li ion being precipitated and ClO_4^- migrating out of the layer was not in accordance with the above results.

In $Li/LiClO_4(PC)/CuF_2$ cells, efficiencies at high currents may be limited by the loss of $LiClO_4$ from the reaction zone due to migration of ClO_4 ion (ref. 8). It was felt that the $Li/LiClO_4(MF)/DCA-70$ cell might have similar limitations. Therefore, a series of cells were discharged from 10 mA/cm^2 to 37.5 mA/cm^2 with several $LiClO_4$ molarities. The data are shown in Table 25.

There is no consistancy in the $i\tau^{1/2}/C$ term, nor any improvement in cell efficiency with increasing $LiClO_4$ concentration. Hence, there is no evidence that our cell is limited due to migration of $LiClO_4$ away from the reaction site. There is, however, some consistancy in the $i\tau^{1/2}$ term. This would be expected if the rate limiting step were the diffusion of DCA-70 to the reaction site. The concentration term, C, is the solubility of DCA-70 in the electrolyte, which is almost constant in these experiments.

b. TCA-85

Voltammetric studies were carried out on TCA-85 to identify similarities with DCA-70, and to try to explain the superiority of the latter material as a depolarizer in non-aqueous electrolyte.

A coulometric experiment was run at 2.5 mA/cm^2 using 0.0215 molar (0.5 g/100 ml) TCA-85. The run lasted 185 minutes (0.463 amp-min.) which was equal to 18.6% efficiency. At this point the voltage dropped sharply and a precipitate was found on the electrode. The analogous experiment using DCA-70 ran 174 minutes (0.436 amp-min.) and 23% efficiency. Thus, the precipitate formed from TCA-85 discharge is not very different in physical form from that of DCA-70.

Table 25

HIGH CURRENT DENSITY DISCHARGE DATA

(10 min P-K blend, 1.5 ml electrolyte)

C.D. mA/cm^2	$LiClO_4$ Molarity	τ >2.0 volts (min)	$i\tau$ (mA-min/cm^2)	$i\tau^{1/2}$	$i\tau^{1/2}/C^*$	Cathode Coulombic Efficiency (%)
10	1.0	70.0	700	83	84	30
10	1.5	95.6	956	97	65	40
10	2.0	144.5	1445	120	60	61
10	3.0	101.5	1015	101	34	43
25	1.0	3.9	98	49	49	4
25	1.5	23.3	563	121	81	24
25	2.0	10.3	258	80	40	11
25	3.0	15.0	375	99	33	16
37.5	2.0	8.1	304	107	54	13
37.5	3.0	5.9	221	91	30	9

* C = concentration of $LiClO_4$ (moles/liter)

2. Chronopotentiometric Studies

a. DCA-70

(1) Platinum Electrode Studies

In conjunction with the coulometric experiments, chronopotentiograms were taken (quiescent solution with currents above the diffusion limit). As shown in Table 26, the chronopotentiograms were regular, and $i\tau^{1/2}$ was proportional to the concentration of DCA-70. Thus, assuming a four electron reduction,* a diffusion coefficient for DCA-70 in 2M $LiClO_4$(MF) can be calculated (ref. 9). The value, $D = 1.4 \times 10^{-6}$ cm^2/sec is similar to values for organic compounds in aqueous solutions. The viscosity of 2.0M $LiClO_4$ was determined in a Cannon-Fenske viscometer tube. The value, $\eta = 1.03$ centistokes per second is also similar to the values for aqueous solutions (e.g., for pure H_2O, n = 1.00 c/s).

Plotting the voltage-time data of the chronopotentiogram indicates that the electrode reaction is quite irreversible. However, there are no gross irregularities in the curve. As shown in Figure 30, the value for αn_a is 0.074 (ref. 9).

A technique of current reversal in chronopotentiometry was developed by Testa and Reinmuth (ref. 10). If a reduction product can be reoxidized at the electrode, then, upon current reversal, one will obtain a chronopotentiometric wave. If the reduction product is insoluble and precipitates on the electrode, the length of time for the reverse chronopotentiogram will equal that of the forward current time (t_a). If the product is soluble and diffuses from the electrode surface, the reverse chronopotentiogram time will be $t_a/3$ with 2/3 of the material diffusing away. If the product is soluble and capable of reoxidation, but enters into secondary reactions (by reaction with solvent or by disassociation), then the reverse chronopotentiogram time will be less than $t_a/3$, and will vary with t_a.

Experiments were performed using this technique with a smooth platinum electrode and silver wire reference electrode. The results are shown in Table 27. Solutions of 0.10M and 0.25M DCA-70 in 2M $LiClO_4$(MF) were used with current densities of 1 to 5 mA/cm^2, and times of 10 to 60 seconds for t_a.

The results indicate that there is an oxidation process upon current reversal. However, the transition time breaks were often not sharp and the voltage difference between oxidation and reduction was large (ca. 1 volt). Where there was no definitive transition break, the values in Table 27 are placed in parenthesis.

* Since similar experiments for TCA-85 give the same diffusion coefficient, assuming n=6 for TCA-85, and battery efficiencies of >50% are achieved for DCA-70, the assumption of n=4 for DCA-70 is undoubtedly correct.

Table 26

DIFFUSION COEFFICIENT OF DCA-70 IN
2M $LiClO_4$(MF) [CHRONOPOTENTIOMETRIC DATA]

Current Density, i (mA/cm^2)	Concentration, C (moles/ℓ)	Transition Time, τ (sec)	$i\tau^{1/2}/C$
2	0.025	28	415
3	0.025	12	415
5	0.025	4	400
5	0.050	15	395
7	0.050	6	345
10	0.050	4	400

$$D = \left(\frac{2\, i\tau^{1/2}}{n\pi^{1/2}FC}\right)^2 = 1.4 \times 10^{-6}\ cm^2/sec$$

assuming n = 4

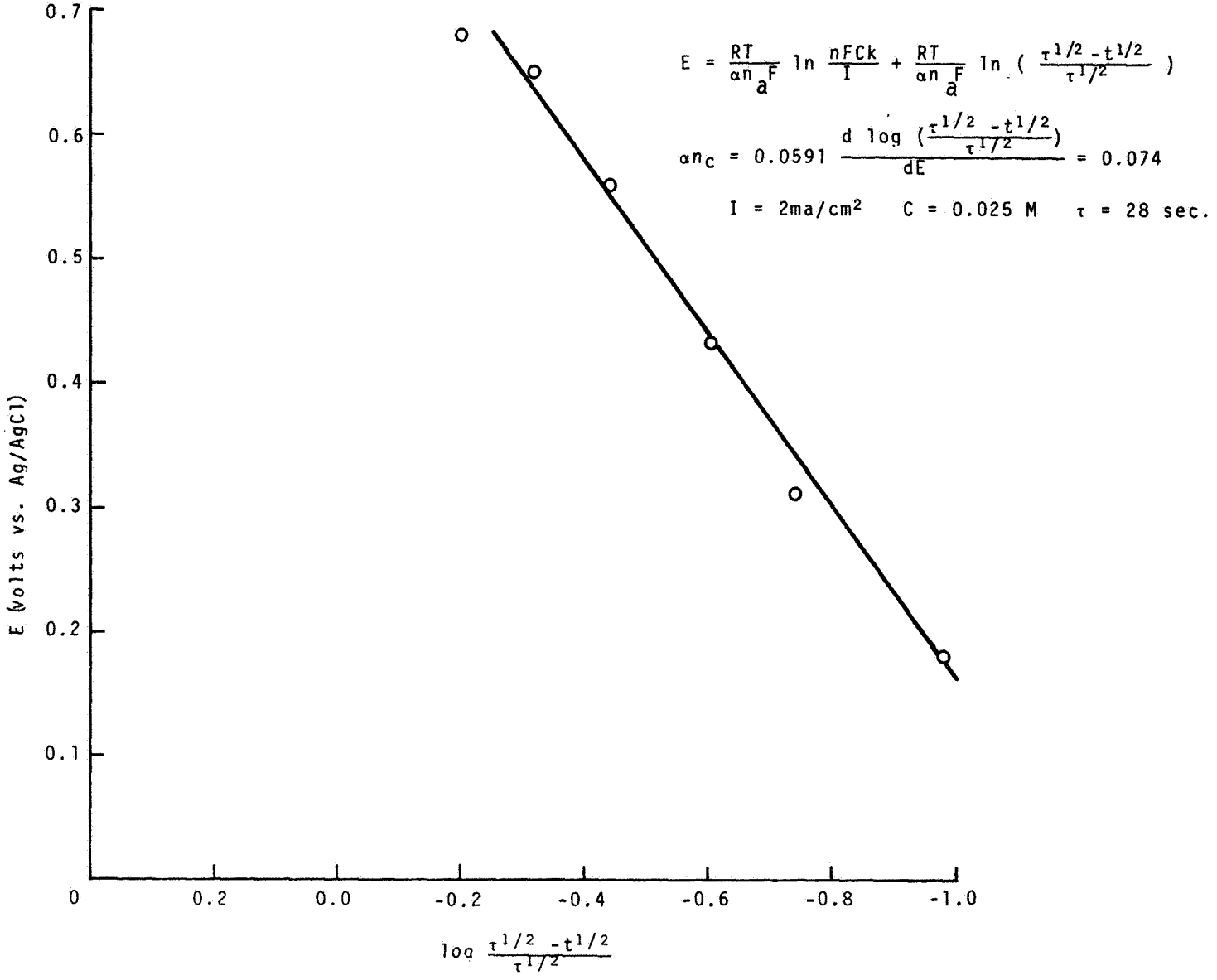


Figure 30. Analysis of Chronopotentiometric Data.

Table 27

CHRONOPOTENTIOMETRY DATA WITH CURRENT REVERSAL

DCA-70 Concentration (M)	Current Density (mA/cm^2)	t_a (sec)	τ (sec)	τ/t_a
0.10	5.0	10	3	0.30
0.10	2.5	20	10	0.50
0.10	2.5	10	6	0.60
0.10	2.5	30	12	0.40
0.10	2.5	60	23	0.38
0.10	1.0	20	(7)*	(0.35)
0.10	1.0	60	(30)	(0.50)
0.10	2.5	30	11	0.37
0.25	1.0	20	7	0.35
0.25	1.0	10	5	0.50
0.25	1.0	30	(13)	(0.42)
0.25	1.0	60	(8)	(0.13)
0.25	2.5	10	(6)	(0.60)
0.25	2.5	20	(10)	(0.50)
0.25	2.5	30	(11)	(0.37)
0.25	5.0	10	3	0.30
0.25	2.5	60	23	0.38

*See text for explanation of parenthesis

The oxidation process may be the regeneration of DCA-70, but the possibility of another processsuchas $2Cl^- \rightarrow Cl_2 + 2e$ cannot be excluded. There is no evidence of a secondary reaction, since the τ/t_a for $t_a = 60$ is as great as for $t_a = 10$. In general, τ/t_a is greater than 0.33 but much less than 1.0. A slow desorption of a soluble reduction product might explain this effect.

(2) Carbon Electrode Studies

Experiments similar to the Pt electrode studies, described above, were carried out with a carbon-epoxy electrode. The inconsistency of the $i\tau^{1/2}/C$ term in these experiments (Table 28) is due to the heterogeneity of the electrode surface and to the slower reaction at carbon. Since $i\tau^{1/2}/C$ was not constant, no definitive calculations can be made. However, a plot of E vs. log $(\tau^{1/2} - t^{1/2})/\tau^{1/2}$ showedno gross irregularity such as might be expected if the reduction occurred at two separate voltages. The curve is shown in Figure 31.

b. TCA-85

Chronopotentiometric experiments were also run using 0.0215 molar (0.5 g/100 ml) TCA-85 solution. The term $i\tau^{1/2}$, was constant, and assuming $n=6$, the diffusion coefficient is $1.4 \times 10^{-6} cm^2/sec$. This is identical to the value found for DCA-70. The voltage-time data were analyzed in a manner similar to that for DCA-70. The curve was regular, giving a value of 0.12 for αn_a. Thus, there is no indication that the reaction is stepwise. Also, the slope of the i f(t) curve indicates a slightly more reversible reduction for TCA-85 than for the DCA-70 ($\alpha n_a = 0.074$ for DCA-70). There is no indication in this data that the reaction kinetics of the TCA-85 discharge limit the TCA-85 cell.

The solubility of TCA-85 was determined in 2M $LiClO_4$ (methyl formate) by the method used for DCA-70. The electrolyte solution, prepared from purified methyl formate, was saturated with TCA-85, and the liquid was analyzed for TCA-85 by an iodine/thiosulfate titration. The solubility of TCA-85 was 28 g/100 ml, which is approximately double the DCA-70 solubility.

Table 28

CHRONOPOTENTIOMETRIC DATA AT CARBON ELECTRODES

Current Density (mA/cm^2)	Concentration of DCA-70 (moles/liter)	Transition Time (τ) (sec)	$i\tau^{1/2}/C$
2	0.050	96	392
3	0.050	26	306
1	0.025	55	296
2	0.025	11	264

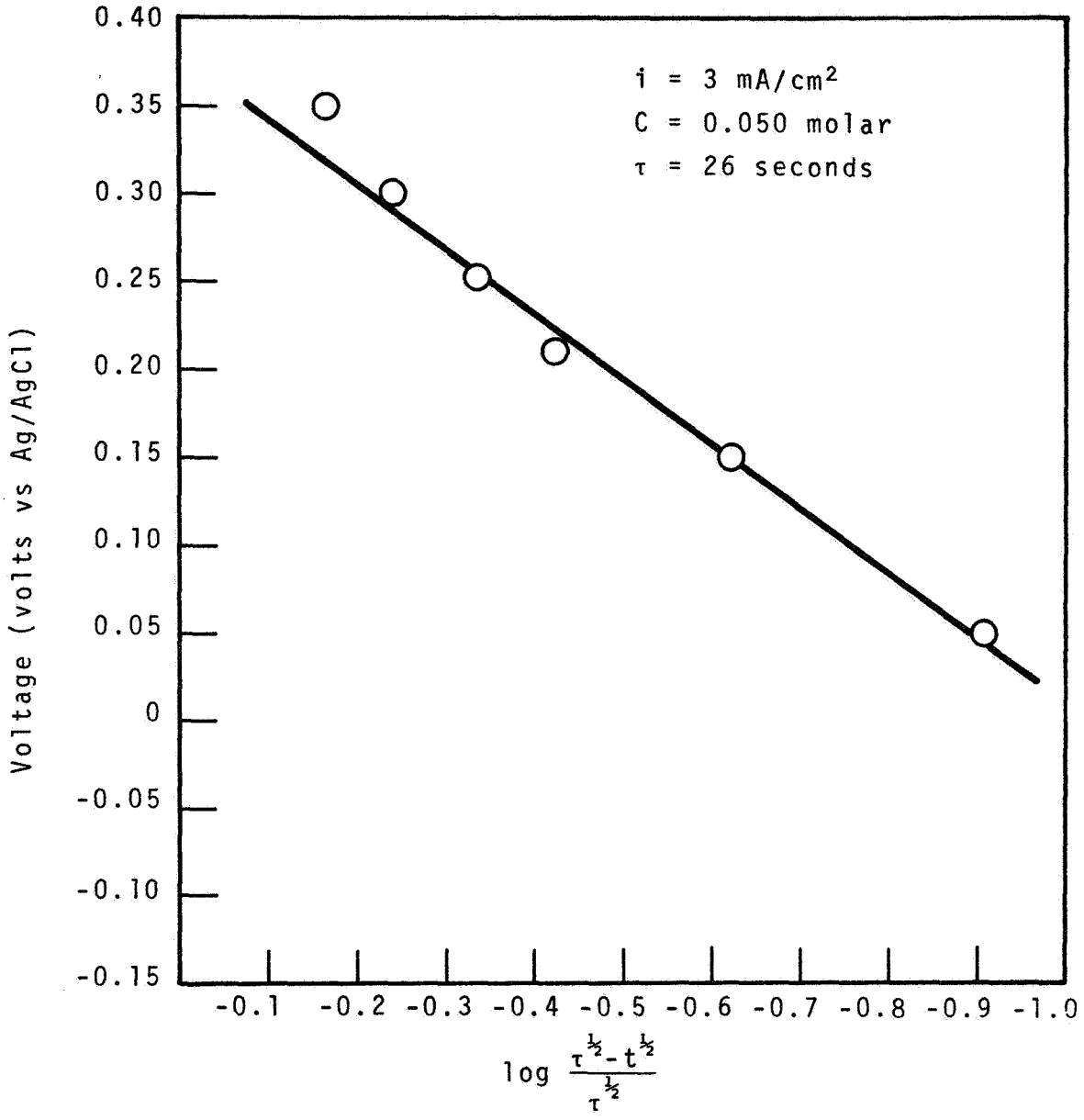


Figure 31. Analysis of Chronopotentiogram of DCA-70 at a Carbon Electrode

D. FULL CELL EXPERIMENTS

1. Cell Performance Data

a. Introduction

Three different discharge conditions were employed for the evaluation of the Li/DCA-70 cell. Constant current discharges, usually at 10 mA/cm^2, were employed for routine screening experiments. Constant voltage tests at 3.2 volts were used to further characterize promising cells, since this type of discharge is characteristic of a Dry Tape discharge (ref. 1). Finally, a limited number of constant load tests were carried out to allow our system to be compared with competitive battery systems.

b. Energy Density as a Function of Various Cell Parameters

(1) Electrolyte Molarity

Earlier work (ref. 1) showed that changes in the $LiClO_4$ electrolyte concentration greatly affected the conductivity and viscosity of the solutions (Figure 32).

The effect of $LiClO_4$ concentration on cell discharge had been considered previously. However, this data (Table 35, ref. 1) only compared results of 2 hour, constant 3.2 volt discharges. Since the effects of viscosity and conductivity might be different at different discharge rates, a concentration study was made at several constant load discharge rates. This data is presented in Table 29. The 1.75M concentration was included because of the maximum in the conductivity to viscosity ratio at this concentration (Figure 4). The data show that high concentrations appear preferable, at least for long discharge times. The 2M, 30 ohm energy density value is low compared to previous data (ref. 1). From previous experience, it appears that no advantage is realized at the 5 hour rate with $LiClO_4$ molarities greater than 2M.

The effect of methyl formate purity is slight (Table 30). The reason for the increase in stability of DCA-70/$LiClO_4$ (Figure 10) is presumably related to the water complexing effect which was reported recently by Dey (ref. 11).

(2) Active Chlorine Compound

Comparison of cell performance based on differences among chlorinated isocyanuric acid derivatives were made with DCA-70, TCA-85 and the lithium salt of DCA-70 ($LiCl_2CYA$).

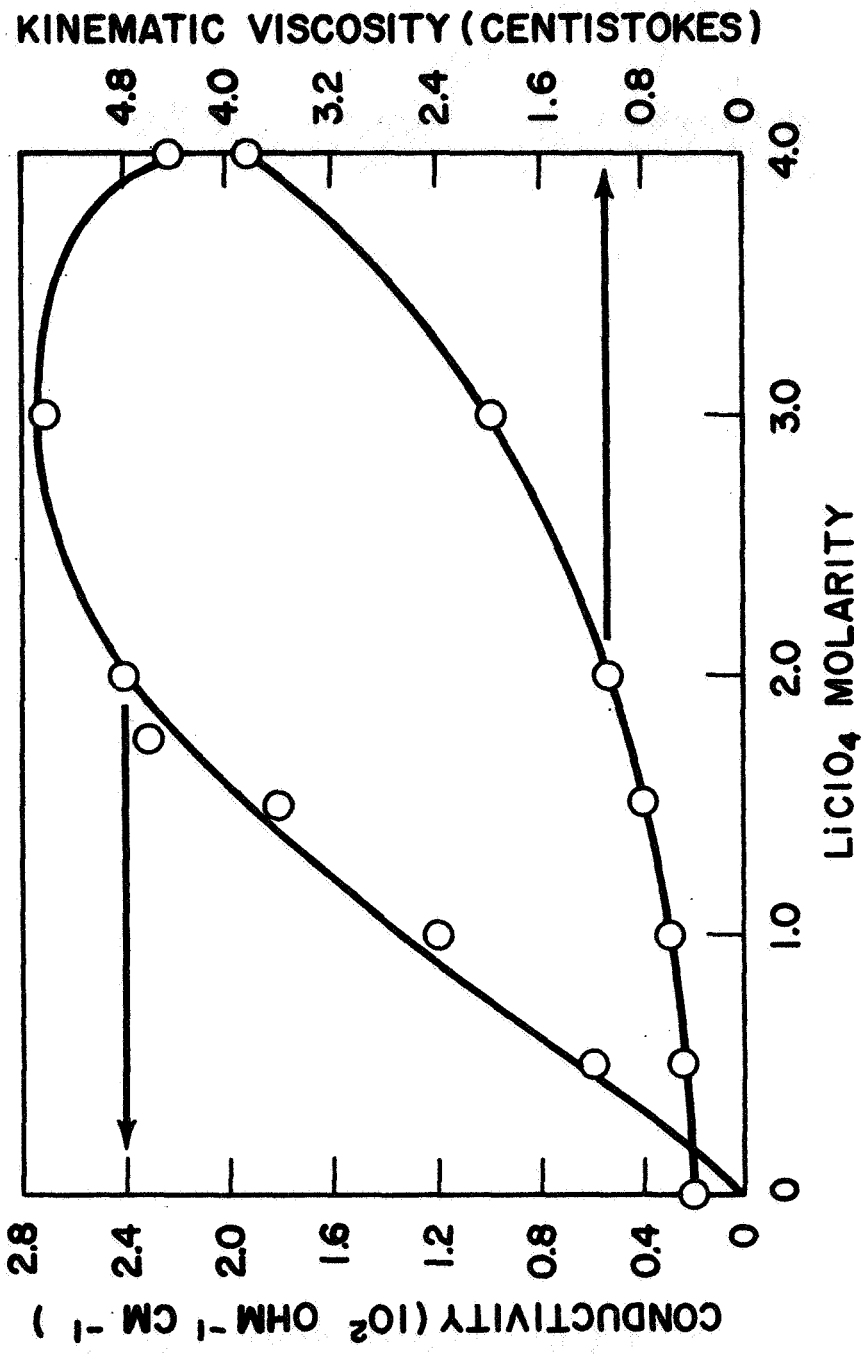


Figure 32. $LiClO_4$(MF) Electrolyte Properties as a Function of Molarity

Table 29

EFFECT OF $LiClO_4$ MOLARITY ON DISCHARGE OF $Li/LiClO_4(MF)/DCA-70$ CELLS

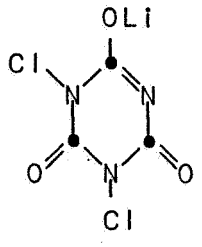
Cell No.	$LiClO_4$ Concentration (moles/l)	Load (ohms)	Discharge Time to 2 volts (min)	Average Potential (volts)	Cathode Efficiency (%)	Energy Density (watt-hr/lb)
105053	1.0	30	222	2.56	39.8	100
105057	1.75	30	245	2.84	48.7	132
105058	2.0	30	273	2.96	57.0	160
105054	3.0	30	295	2.96	62.9	171
105055	3.0	9	67	2.69	59.4	112
105056	3.0	124	1162	3.17	62.0	180

Table 30

DISCHARGE OF Li/2MLiClO$_4$(MF)/DCA-70 CELLS

(20 Ohm Load)

Cell No.	Electrolyte Type	Electrolyte Volume (ml)	Discharge Time to 2 volts (min)	Average Potential (volts)	Cathode Efficiency (%)	Energy Density (watt-hr/lb)
105058	Purified	1.4	273	2.96	57.0	160
105059	Standard	1.4	282	3.07	60.3	176
105060	Standard	1.5	290	3.10	61.8	176
105062	Standard	1.5	281	3.08	60.7	172
105064	Purified	1.5	292	3.08	62.1	176



($LiCl_2CYA$)

These cells were discharged in the jelly-roll configuration in a gas tight cell holder.

The gas tight cell necessitated the use of a 50% excess of electrolyte relative to our research cell. This decreased the energy density (Table 31). In one test, 3.50 ml was used in place of the 4.25 ml normally used. In the present cell design, 3.50 milliters is apparently too little, since the cell efficiency decreased sharply. The cells were discharged through a 20 Ω resistor. Gassing (Section II.D.3), as well as electrical data were obtained. DCA-70 is superior to TCA-85 or $LiCl_2CYA$. This superiority is not due to solubility characteristics (Table 32).

(3) Cathode Thickness

Normal thickness of the cathode is 0.045 inch. Therefore, weights were doubled and quartered to achieve nominal 0.010" and 0.10" thicknesses. Results are given in Table 33 for 10 mA/cm^2. The 0.01" thickness was not easily obtained in a uniform 20 cm^2 area. The 0.10" thickness was run in duplicate because of a possible error. Based on this data, the 0.05" thickness was used for screening experiments.

(4) Current Density

Using the standard cathode thickness (0.05 inch), a series of current densities were tested. This data is shown in summary form in Table 34. A value of 10 mA/cm^2 was chosen as the highest current density which would give good performance at the standard thickness.

By decreasing the cathode thickness, higher current densities and much higher discharge rates were obtained. Data on these thin cathodes are given in Table 35. The carbon black content in these studies is 28%. Energy density values range from 69 w-hr/lb for the 6 minute rate to 90 w-hr/lb for the 30-60 minute rate.

Table 31
Effect of Cyanuric Acid Compound on Discharge

Cell	Active Material	Electrolyte Vol (ml)	Load	Discharge Time to 2 volts (min)	Average Potential (volts)	Cathode Efficiency (%)	Energy Density (w-hr/lb)
105065	DCA-70	3.50	20	286	3.18	47.4	127
105070	DCA-70	4.25	20	374	3.30	64.5	161
105071	$LiCl_2CYA$	4.25	20	226	2.73	32.2	67
105072	$LiCl_2CYA$	4.25	20	221	2.73	30.1	63
105073	TCA-85	4.25	20	280	2.54	27.7	70

Table 32

THE SOLUBILITY OF CHLORINATED ISOCYANURIC ACIDS IN 2M $LiClO_4$-MF ELECTROLYTE AT 22°C

Depolarizer	Solubility (g/100 ml)
$LiCl_2CYA$	2.8
DCA-70	14
TCA-85	28

Table 33

EFFECT OF CATHODE THICKNESS ON DISCHARGE
(17% Carbon, 0.5 min WB, 10 mA/cm^2, 20 cm^2)

Cell No.	Thickness (inches)	Capacity (amp-min)	Average Volt(v)	Efficiency (%)	Energy Density (w-hr/lb)
105100	0.01	11.81	3.23	33.0	69
109314	0.05	47.25	2.77	52.1	133
109316	0.05	47.25	3.15	58.1	168
109307	0.10	94.50	3.29	13.9	46
109308	0.10	94.50	3.00	15.9	48

Table 34

EFFECT OF CURRENT DENSITY ON DISCHARGE
(17% Carbon, 0.5 min WB, 47.25 amp-min, 20 cm^2)

Cell No.	Current Density (mA/cm)	Average Volt(v)	Efficiency (%)	Energy Density (w-hr/lb)
109306	1	3.36	60.3	187
109305	5	3.28	57.1	173
109316	10	3.15	58.1	169
109304	25	2.78	10.9	28
109314	10	2.77	52.1	133

Table 35

CONSTANT CURRENT - HIGH RATE DATA

Cell No.	Concentration ($g/20cm^2$) DCA-70	SAB	Current Density (mA/cm^2)	Cathode Efficiency (%)	Discharge Time to 2.0 volts (min)
109377	0.50	0.30	10	63	50
109378	0.50	0.30	15	64	33
109379	0.50	0.30	20	64	25
109380	0.50	0.30	25	59	18
109381	0.17	0.10	25	54	6

The current densities range from 10 to 25 mA/cm^2. The cathode thickness for 0.5 g DCA-70 is 0.032 inch. For the 6 minute rate, the cathode thickness is presumed to be 0.010 inch. In these tests, a considerable weight penalty must be absorbed for the 0.015 inch lithium strip.

(5) Carbon Content

Some experiments were performed to further assess the effect of increasing void volume by increasing the carbon content, and by decreasing the formation or test pressures. These experiments are summarized in Table 36. Cells 109263 and 109282 show that by increasing the carbon content, a higher cathode efficiency is obtainable. However, this increased carbon content does not allow the cell to be discharged at a higher rate, and a large increase in electrolyte volume is required. The effects of decreasing the test and formation pressures are marginal.

By visual observation, it was felt that crystal formation might be partially disconnecting the cell by masking the current collector plate. In Cell 109262, a high-conductivity graphite (Micro 6-Asbury Graphite Mills) was laid on top of the platinum collector plate. This gave both a reservoir for electrolyte at the base of the cell, and a porous base that conformed to the cathode face. In this way the crystal growth on the collector side should be avoided. Cell 109262 showed no major increase in cathode efficiency.

Table 36

CATHODE VARIATIONS - CARBON PERCENT AND ELECTROLYTE VOLUME

Cell	Carbon (%)	Pressure (psi) Forming	Pressure (psi) Testing	Electrolyte (ml)	C.D. (mA/cm^2)	Average Voltage (V)	Efficiency (%)	Energy Density (w-hr/lb)
109257	17	300	5.3	1.8	10	3.13	55.9	148
109259	17	100	5.3	1.8	10	3.09	59.8	157
109263	25	300	5.3	2.5	10	3.10	62.7	134
109282	25	300	5.3	2.5	25	2.58	27.7	49
109262	17*	300	8.0	1.7	10	3.12	59.7	162
109258	17	300	8.0	1.5**	10	2.78	42.9	106
109297	15***	300	8.0	1.7	10	3.25	49.5	135

*Porous graphite base used
**3M $LiClO_4$; 2M used in other tests
***0.15g $LiPF_6$ added to cathode mix

By increasing the Shawinigan acetylene black (SAB) content to 28% from 17%, the cathode efficiency increased only slightly. Since the cathode could be discharged with 17% SAB, other carbons were incorporated to increase the carbon content to 28%. These carbons were (1) the high surface area Darco G60 charcoal, and (2) the Columbian battery black Conductex-SC ($220 m^2/g$). These high surface area blacks did not improve the cell performance (Table 37).

High electrolyte molarity (3M $LiClO_4$) did not improve the operation of the cathode at 10 mA/cm^2. In Cell 109297 (Table 36), a soluble salt, $LiPF_6$, was added to the cathode mix. This salt could dissolve and generate anions for migration. While the cell performance indicated no improvement of cathode efficiency at 10 mA/cm^2, the average voltage (3.25) was significantly higher than normal, and this was presumably due to improved conduction (decreased IR loss) in the cathode.

(6) DCA-70 Particle Size

During our blending studies (Section II.B), it was shown that increased mixing of carbon and DCA-70 decreased the cell performance. Therefore, experiments were undertaken to decrease the initial size and agglomerates of DCA-70 and carbon prior to blending, so that shorter mixing times could be used. Decreasing the DCA-70 particle size might also increase the availability of DCA-70 at the reaction site, leading to higher current density operation.

The DCA-70 was screened through a 50 mesh Teflon coated metal screen, then through 100, 325, and 400 mesh nylon screens. A slurry technique was used to pass the DCA-70 through the finer screens. The large particles of DCA-70 were primarily aggregates. Almost all of the primary particles are smaller than 325 mesh.

Because of the fragility of the DCA-70 agglomerates, the Waring blender could not be used without further size reduction. Therefore, 10 minutes of P-K blending was used. Data are given in Table 38.

The large agglomerates (cell 109337) give poorer performance than smaller particles.

(7) Pressure and Electrolyte Requirements

From the data above, the better blending methods and carbon preblending methods yield mixes which required larger electrolyte amounts. It is possible that the apparent efficiency improvement is due to the presence of extra electrolyte. Another way in which the amount of electrolyte required is increased, which does not require changing the blend, is a decrease in the cell test pressure. The data in Table 39 indicates, again, that electrolyte absorption is perhaps the critical parameter.

Table 37

EFFECT OF VARIOUS CARBON BLACKS ON CELL PERFORMANCE
(10 mA/cm^2)

Cell No.	Carbon Content (g/20cm^2) SAB	Other	Electrolyte (ml/20cm^2)	Cathode Efficiency (%)
109246	0.28	0.02*	1.5	58.6
110780	0.50	-	2.3	62.6
110786	0.30	0.20**	2.1	61.0
109368	0.30	0.20**	2.0	61.4
110779	0.30	0.20***	2.0	59.2
110796	-	0.50**	1.9	4.2
110797	0.20	0.30**	1.9	15.2

* Carbon Fibers
** Conductex SC
***Darco G-60

Table 38

EFFECT OF DCA PARTICLE SIZE ON CELL DISCHARGE
[10 min P-K blend, 1.5 ml, 2.0M $LiClO_4$(MF), 10 mA/cm^2]

Cell	DCA-70 (mesh size)	Average Voltage(V)	Efficiency (%)	Energy Density (w-hr/lb)
109312	>400*	2.99	54.8	151
109336	100-325	3.22	50.2	149
109337	<50	3.17	42.5	124

*DCA-70 after mortar and pestle grinding is primarily smaller than 400 mesh. Hence, the normal DCA-70 sample is of this size.

Table 39

EFFECT OF ELECTROLYTE AMOUNT AND PRESSURE ON CELL DISCHARGE
(1 hr P-K blend)

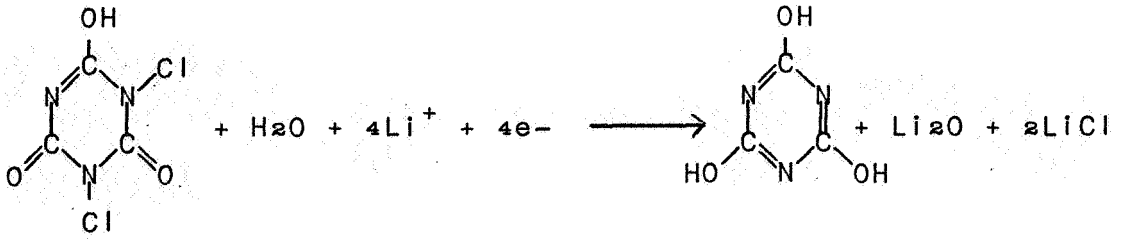
Cell	Electrolyte (ml)	Test Pressure (psi)	Average Voltage(V)	Efficiency (%)	Energy Density (w-hr/lb)
109309*	1.5	8	3.06	51.2	145
109251	1.7	8	3.15	54.5	150
109253	1.7	5.3	3.09	59.1	159
109257	1.8	5.3	3.13	55.9	148

(8) DCA-70 Purification

As described in a following section (II.D.4), commercial DCA-70 was found to be not chemically pure. By removing the MF-insoluble fraction ($NaCl_2C_3N_3O_3$), it was felt that the cell performance might be improved. However, this was not the case (Table 40).

The insoluble fraction discharged similarly to the soluble fraction and a recombination of soluble and insoluble fractions did not cause a recovery in performance relative to that of the commercial material. Therefore, an alternative hypothesis might be that recrystallization of the DCA-70 removes a necessary impurity. This impurity could be water. Our standard DCA-70 drying technique, (vacuum, over P_2O_5, after grinding with mortar and pestle) however, should remove most of the water. One test was made with DCA-70 without the drying step. The result indicated an improvement with undried DCA-70.

Water may improve performance by allowing the reduction product to be converted to cyanuric acid in our aprotic electrolyte. However, this would require 0.14g H_2O for 1.5g DCA-70 according to the following equation:



$$HCl_2C_3N_3O_3 + H_2O + 4Li \longrightarrow H_3C_3N_3O_3 + Li_2O + 2LiCl$$

Table 40

EFFECT OF DCA-70 PURITY ON CELL DISCHARGE CHARACTERISTICS
(10 mA/cm^2, 28% SAB)

Cell No.	DCA-70 Sample Source	DCA-70 Sample amp-min/g	Efficiency (%)	Energy Density (w-h/lb)
110780	std[1]	31.5	62.6	146
109368	std	31.5	61.4	155
110781	sol[2]	32.6	59.7	141
110792	sol	32.6	59.1	138
110795	sol	32.9	42.7	95
109375	sol	32.9	45.4	109
109369	insol[3]	26.8	61.2	99
109382	sol 90%[4] insol 10%	32.9 26.8	51.4	111
109384	std undried	31.9	65.2	150
109390[5]	std undried	31.9	64.2	145

(1) Standard commercial sample
(2) The MF soluble fraction
(3) The MF insoluble fraction
(4) Recombination of separated fractions
(5) SAB exposed to water vapor

It is also possible that an impurity (e.g., H_2O) may be required to passivate the lithium surface towards self-discharge reactions. Therefore, after a discharge with soluble DCA-70 (109385) the cathode was analyzed for the active chlorine remaining. A total of 13% capacity was lost. This is much greater than when standard DCA-70 is used.

Cell 109390 was discharged with undried standard DCA-70, and with humidified carbon black. The water uptake of carbon was 3 mg H_2O/g SAB, which increased the cell water content by only 1.4 mg. The cell discharge was not quite as good as with the undried DCA-70 cell, but it was significantly better than the discharges using dried or recrystallized DCA-70. The cell was disassembled at the end of the discharge and the cathode titrated for the remaining active chlorine content. Only 63% of the active chlorine could be accounted for. These results indicate that the required impurity in DCA-70 stabilizes the cathode, probably by passivating the anode toward reaction with soluble DCA-70.

c. DCA-70 Liquid Cathode Reductions

The above data suggests that an increase in the percentage of carbon and electrolyte gives an increase in the efficiency of cell operation. There is also some evidence that the rate limitation is due to diffusion of DCA-70 to the reaction site. For this reason, DCA-70 dissolved in 2M $LiClO_4$ was used as the oxidizing agent in the discharge of Li/C cells. The results of these discharges are shown in Table 41. Figure 33 shows a typical discharge curve from this series. In these experiments, the DCA-70 and electrolyte were added to the cathode and separator. There is some gassing and reaction of the lithium anode with the 15 wt-% DCA-70 solution. However, the reaction is not violent. From these results it is evident that current densities higher than 25 mA/cm^2 are impractical even with the DCA-70 pre-dissolved and added to 100% carbon. The cathode efficiencies of these cells at 10 mA/cm^2 are 40%, and only 10% of the active material remains in the cathode after discharge. Finally, the efficiency improves when thicker cathodes are used. One of these cathodes was microtomed. No product crystals could be observed.

Figure 33 shows that the discharge of dissolved DCA-70 is not a simple process. We ascribe the complexity to complex formation in the precipitation of products within the cathode, since the chronopotentiograms of dissolved DCA-70 were simple and showed no voltage plateaus. Coulometric experiments gave precipitates and complex voltage curves.

d. Constant Voltage Tests

Under a previous contract (ref. 1), we obtained test cell energy densities in excess of 200 watt-hr/lb, based on weights of tape and electrolyte. These constant voltage values were 10% higher than those obtained at constant load. The dynamic discharge of a Dry Tape segment is at constant voltage. For this reason, several static, constant voltage tests were performed to assess any improvement in cathode efficiency and discharge rate produced by changes suggested by this year's testing program. One improvement carried throughout this program was the use of methanol-free methyl formate which is obtained by passing the solvent through a column of Linde 4A molecular sieves.

An excess of electrolyte was generally used in these tests since the objective is an increase in rate and efficiency, rather than the energy density. The complete data are given in Appendix Table A-6, while summary data are presented in Tables 42 and 43.

Table 41

CONSTANT CURRENT REDUCTION OF DCA-70 SOLUTIONS

(15 weight-% DCA-70 in 2M $LiClO_4$-MF)

Cell	Carbon ($g/20\ cm^2$)	Oxidizing Solution ($ml/20\ cm^2$)	C.D. (mA/cm^2)	Cathode Efficiency (%)	DCA-70 Unreacted (%)
109289	0.60	3.0	10	40	10
109290	0.60	3.0	25	28	--
109292	0.30	1.3	10	26	--
109294	0.30	1.3	5	36	10
109296	0.30	1.3	5	29	--

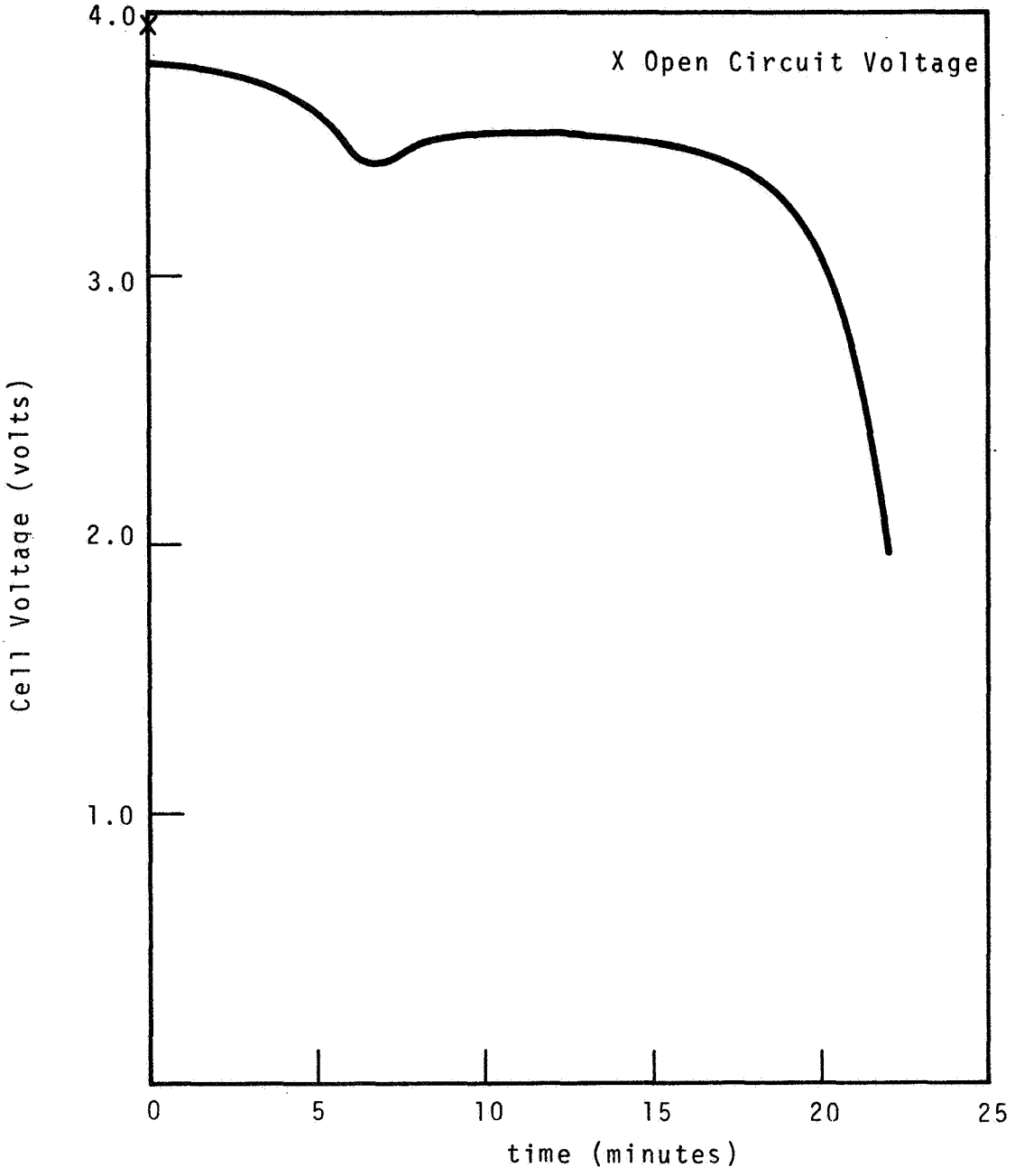


Figure 33. Discharge Curve for Reduction of Dissolved DCA-70 (Cell 109294)

Table 42

EFFECT OF ELECTROLYTE, VOLTAGE AND CARBON CONTENT ON THE EFFICIENCY OF Li/DCA-70 CONSTANT VOLTAGE DISCHARGE

(1.5 g DCA-70, 0.5 min WB, 8 psi Test Pressure)

Cell No.	% Carbon	Electrolyte Type	Electrolyte ml	Voltage (V)	Efficiency (%) 1 hr	Efficiency (%) 8 hr
109343	17	2M $LiClO_4$	1.5	3.2	33.5	64.0
109345	17	2M $LiClO_4$	1.5	3.0	33.2	59.2
109347	25	2M $LiClO_4$	2.5	3.2	32.1	58.9
109348	25	2M $LiClO_4$	2.3	3.2	38.7	68.0
109342	17	2M $LiAsF_6$	1.5	3.2	24.5	60.9
109357	17	3M $LiAsF_6$	1.5	3.2	31.0	60.4
109358	17	3M $LiAsF_6$	1.45	3.2	28.0	58.2

Table 43

EFFECT OF BLENDING AND PRESSURE ON THE EFFICIENCY OF 3.2 VOLT Li/DCA-70 DISCHARGES

[1.5 g DCA-70, 17% Carbon, 2M $LiClO_4$ (MF)]

Cell No.	Blend Type	Blend min.	Test Pressure (psi)	Electrolyte Volume (ml)	Cathode Efficiency(%) 1 hr	Cathode Efficiency(%) 8 hr
109343	WB	0.5	8	1.5	33.5	64.0
109351	WB	0.5	8	1.4	32.8	64.5
109346	WB	0.5	5.7	1.7	33.6	64.8
109349	WB	0.5	5.7	1.5	33.2	62.5
109350	WB	0.5	5.7	1.4	29.3	52.3
109354	WB	0.16	8	1.5	34.7	68.7
109356	WB	0.16	8	1.4	32.2	64.6
109353	PK	10	8	1.5	31.6	67.6
109355	PK	60	8	1.5	34.2	67.4

Test 109343 is the standard for the series. Decreasing the voltage (3.0v vs. 3.2v) should increase the rate of electrochemical limiting processes. However, the test (109345) shows no improvement in rate of discharge.

Increasing the amount of carbon might also increase the efficiency and rate since the cell would have more electrolyte and better electronic and electrolytic conductivity. An increase from 17 to 24% carbon did show a significant efficiency increase at high rate (109348); but the weight penalty was large. At 1 hour, the standard cell energy density is 99 w-h/lb and the 24% carbon cell is 89 w-h/lb; the efficiencies are 13.5% and 38.7% respectively.

The conductivity of the electrolyte could be an important parameter in determining the maximum rate of discharge in organic electrolyte systems. Since the conductivity of $LiAsF_6$ is considerably greater than that of $LiClO_4$, three cells were discharged with $LiAsF_6$. As in previous tests, there was no advantage to the use of $LiAsF_6$ over $LiClO_4$.

The effect of blending and pressure is shown in Table 43. With less test pressure, more electrolyte is required. However, no significant increase in efficiency is observed, (tests 109343, 51,46,49-50). From previous analysis of blending, a short mixing time was found to be beneficial. Thus, 10 second Waring blending of carbons plus 10 second blending of carbon with DCA-70 was used (see also Cells no. 109338, 40, 46, 47). Finally, two of the short time Patterson-Kelly Twin Shell blends were studied. The results show an improvement only for the 10 second Waring blending. Visual observation shows that the short time P-K blends are not well mixed. This result suggests that a direct vortex dry solids unit (Sprout-Waldron Co.), might give some excellent mix for large quantity applications. The unit uses compressed air pulses to achieve mixing with suggested mixing times of 16-60 seconds. The quantity of DCA-70 presently required might be a safety hazard, however.

Final optimization of the cathode mix for constant voltage discharge can be seen in the data of Table 44. The best result, using 5 seconds carbon fluffing plus 5 seconds blending of DCA-70 and carbon, is significantly better than the standard 60 second carbon blending, and 30 second DCA-70-carbon blending (110763 vs. 109343).

Table 44

CONSTANT VOLTAGE DISCHARGE DATA
(3.2 volts)

Cell No.	Amount DCA-70 (g)	Amount Carbon (%)	Amount Electrolyte (ml)	Blending Time(sec) Carbon	Blending Time(sec) Total	Cathode Efficiency(%) 1 hr	Cathode Efficiency(%) 8 hrs
109343*	1.5	17	1.5	60	30	33.5	64.0
109348*	1.5	25	2.3	60	30	38.7	68.0
109354*	1.5	17	1.5	10	10	34.7	68.7
109360	0.9	25	1.4	60	30	52.3	70.2
109361	1.5	17	1.5	10	10	33.0	68.7
110757	1.5	17	1.5	0	5	31.0	67.3
110763	1.5	17	1.5	5	5	34.2	69.5
109363	1.5	25	2.3	5	5	36.8	71.0
109365	0.9	25	1.4	5	5	51.6	74.8
109367**	1.5	17	1.5	10	10	38.1	69.5
109371***	1.5	17	1.6	10	10	36.1	66.8
110763	1.5	17	1.5	5	5	34.2	69.5
110785***	1.5	17	1.5	10	10	10.0	53.8
109372	0.5	38	1.2	10	10	63.5	74.1

* Data from Report No. 11
** Soluble fraction of DCA-70. Efficiency based on 31.1 amp-min/g.
*** Soluble fraction of DCA-70. Efficiency based on 32.6 amp-min/g.

When increased carbon content (25% vs. 17%) was employed, the cell required more electrolyte and was considerably thicker than the standard cell. Two tests were made with 25% carbon in which the DCA-70 quantity was decreased, rather than the carbon increased. These tests show a large improvement in cathode utilization, especially at short times. Efficiencies of over 50% are obtained within one hour at 3.2 volts in these tests. The 75% efficiency achieved in 8 hours is the highest utilization achieved on this program. The energy density calculated at 1 hour is 112w-hr/lb.

DCA-70, as obtained, is not completely soluble in methyl formate(no $LiClO_4$). The insoluble fraction is the sodium salt of DCA-70 (see Section II.D.2). Although this salt is soluble in our electrolyte [2M $LiClO_4$(MF)] it may not be reduced as effectively as DCA-70. Also the large quantity of Na ion may decrease the electrolyte conductivity or otherwise inhibit performance of the cell.

Soluble batches of purified DCA-70 were obtained by extraction with methyl formate and used for a cell discharge. The first batch of material had a coulombic capacity of 31.1 amp-min/g, whereas the commercial product analyzed at 31.5 amp-min/g. The pure compound should have a 32.5 amp-min/g capacity. Hence, some decomposition probably occurred in the re-crystallization process. Purer samples were later prepared. The cell discharge characteristics of the first material showed a considerable improvement in cell performance, especially at short times. However, with purer samples this improvement was not found. This may be related to the more complete removal of a necessary impurity, as discussed in the previous section.

e. Constant Load Tests

Discharges at the 1 and 3 hour rates were performed using the 10 minute P-K blend mix with 9 and 20 ohm resistors. The results, shown in Table 45 are comparable to the data shown in our earlier work (ref. 1), for the 1 and 3 hour rates. There is no improvement based on this blending method.

Table 45

CONSTANT LOAD DISCHARGE OF 10 MINUTE P-K BLENDS
[1.5 ml, 2.0M $LiClO_4$(MF)]

Cell	Load (ohms)	Time to 2.0v (min)	Average Voltage(v)	Efficiency (%)	Energy Density (w-hr/lb)
109321	9	68	2.82	44.9	117
109322	20	167	3.13	55.0	159

2. Analysis of Cathode Discharge Products

a. Introduction

Analysis of the electrochemical discharge of the Li/DCA-70 system indicated that an insoluble product (see Section II.C) is formed in the cathode. In addition, the relatively soluble depolarizer (DCA-70) is not consumed in self-discharge. The cell inefficiency therefore, results from DCA-70 (or some active chlorine compound) which is not available for reduction. Changes in chathode preparation and electrolyte conductivity make only secondary changes in the cell efficiency. Although a large increase in carbon and electrolyte does improve the efficiency, none of these changes increase the maximum rate of discharge.

Based on these factors, the most reasonable explanation for the efficiency and rate limitations in the Li/DCA-70 cell is an insoluble cathode product which severely limits DCA-70 diffusion.

Therefore, a program was carried out to identify and characterize the products of the Li/DCA-70 cell reaction. This information might lead to logical changes in the cathode or electrolyte which would improve the cell efficiency and the maximum rate of discharge. The products were pursued in three ways, (1) cathode extraction, (2) electrochemical synthesis and (3) chemical synthesis.

b. Identification of Cathode Reduction Products

(1) Extraction of Discharged Cathodes

Since DCA-70 and LiCl are both somewhat soluble in methyl formate, and the DCA-70 reaction product was presumed to be insoluble, a discharged cathode was extracted in a Soxhlet extractor with methyl formate in order to partially separate the components. The extraction should leave the carbon and organic reduction product as the remaining solids. Different samples of this residual solid were then extracted with acetone and with acetonitrile. Both extractions gave products which were isolated by evaporation of the solvent. Both of these products had the same infrared spectrum (Figure 34), which was similar to (1) the spectrum of the product from a platinum electrode coulometric experiment (see Figure 14b) and (2) to the decomposition product of DCA-70 in standard methyl formate (Figure 13a). While this material cannot be positively identified, its infrared spectrum is very similar to that of a spectrum of cyanuric acid in the literature (ref. 12).

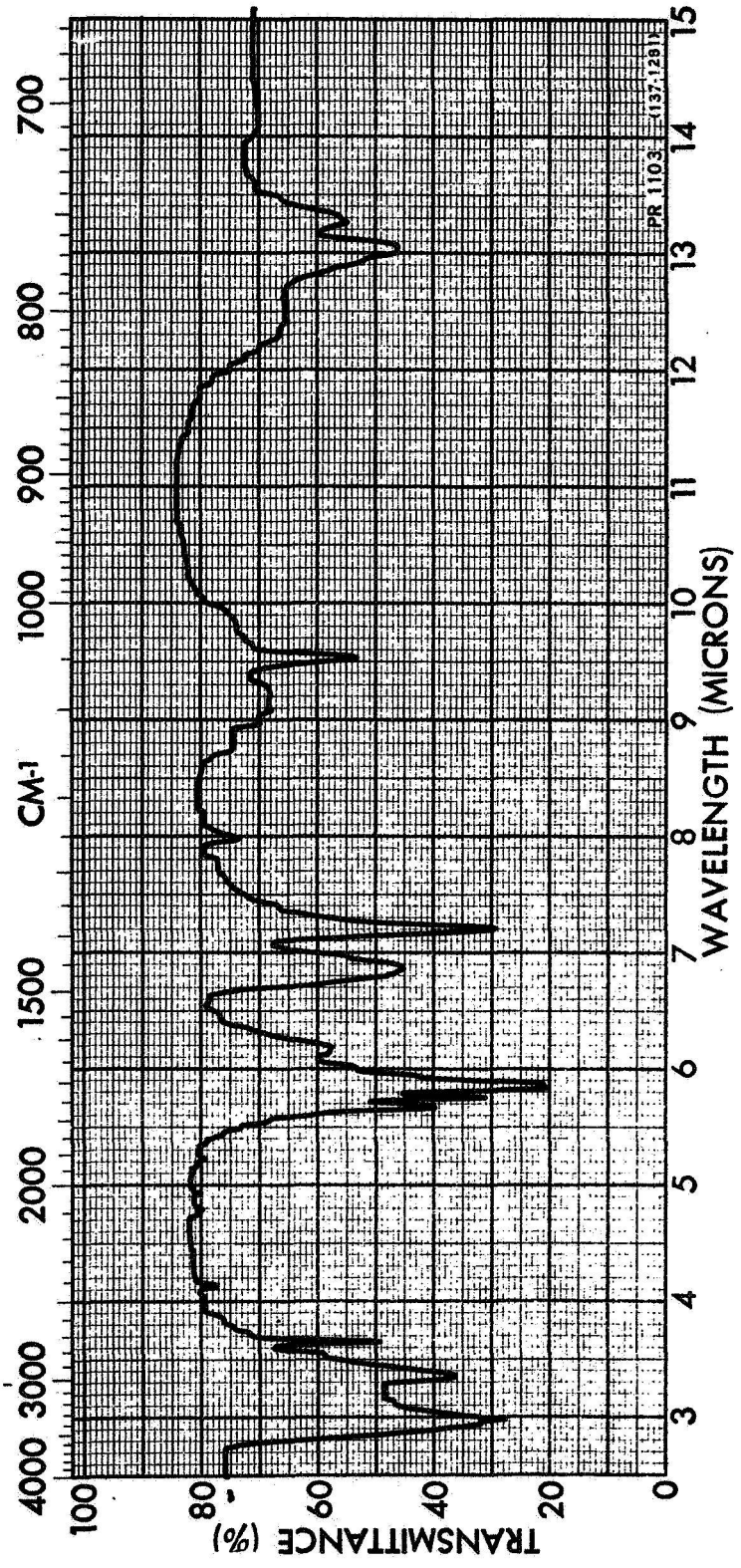


Figure 34. Infrared Spectrum (KBr Pellet) of the Product Extracted with Acetone from a Discharged Cathode

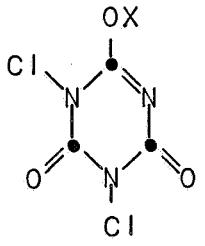
A sample of discharged cathode was submitted for x-ray analysis, primarily to determine the presence or absence of Li_2O. The presence of Li_2O could indicate the breakdown of the lithium salt of cyanuric acid into Li_2O and a polymer of cyanuric acid with ether linkages. No Li_2O was found in the x-ray pattern. However, a sharp line at d = 3.03 was observed which is unexplained.

(2) Electrode Discharge Products

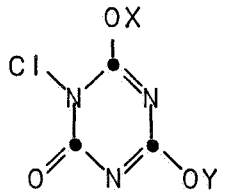
During a series of experiments to assess the coulombic acceptance capacity of a carbon rod electrode prior to electrode blockage, enough material was obtained to make a KBr pellet for infrared spectral analysis. The spectrum is shown in Figure 35. It is identical to the spectrum of the cathode extraction experiment (Figure 34). This experiment was performed with dried MF and $LiClO_4$ and the electrolyte should not contain sufficient water to give cyanuric acid. It is not known, however, how much water is available from the KBr.

(3) Chemical Synthesis of Cyanuric Acid Salts

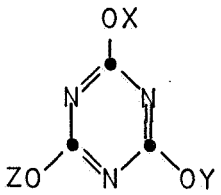
A number of triazine derivatives are reasonable candidates as ACL-70 reaction products. These compounds can be classified as derivatives of dichloroisocyanuric acid (A), monochloroisocyanuric acid (B), and cyanuric acid (C).



(A) X = H,Li



(B) X = H,Li
Y = H,Li



(C) X = H,Li
Y = H,Li
Z = H,Li

There are 2, 3 and 4 derivatives of A, B and C, respectively. We had available both derivatives of (A). The monochloro derivatives (B) are unstable, unknown, and would probably be further reduced under the reaction conditions. We had available cyanuric acid [(C), X = Y = Z = H], and set out to prepare the other three derivatives of (C), i.e., the mono-, di- and trilithium salts of cyanuric acid. These derivatives of (C) are most logical as cathode reaction products in our non-protonic electrolyte system.

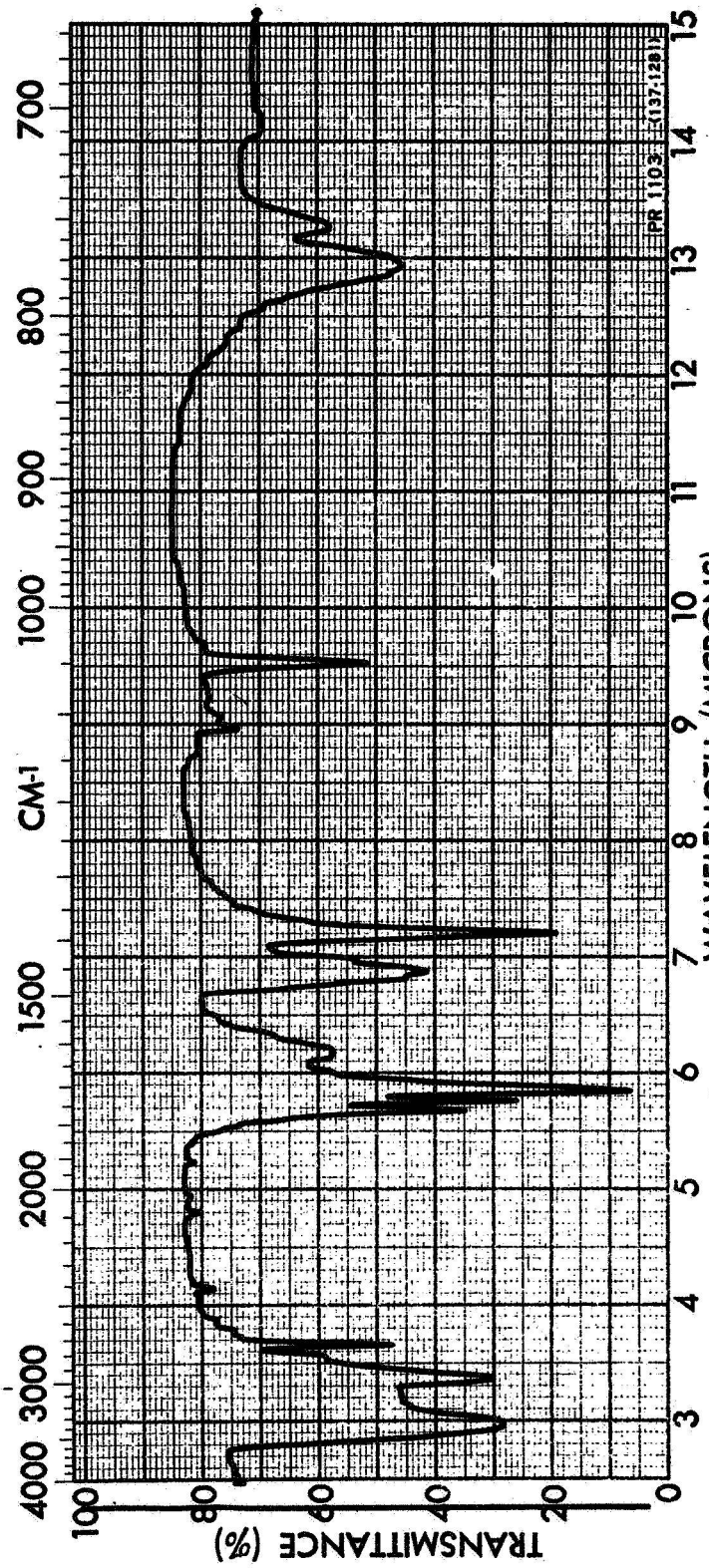


Figure 35. Infrared Spectrum (KBr Pellet) of the Product Obtained from the Electrochemical Reduction of DCA-70 at a Carbon Electrode

The most likely product of DCA-70 reduction is the dilithium salt of cyanuric acid ($Li_2HC_3N_3O_3$). Another possibility, especially for the Li + DCA-70 self-discharge reaction, is $Li_3C_3N_3O_3$. Therefore, it would be desirable to have these compounds prepared and characterized.

Cyanuric acid ($H_3C_3N_3O_3$) was suspended in water and titrated with LiOH in an attempt to synthesize these products. Titration with one equivalent of LiOH gave a sharp pH change which could be used to assay the $H_3C_3N_3O_3$ purity (100.5%). There were no further pH steps to indicate further product formation. Products were isolated from the $H_3C_3N_3O_3$ plus 1, 2 and 3 LiOH equivalents. The infrared spectra from the reaction of 1 and 2 equivalents are different, indicating that the mono and dilithium salts were formed. The $Li_3C_3N_3O_3$ derivative was not formed. The lithium salts were very soluble in water and were collected by evaporating solutions to dryness. Hence, no digestion step should be necessary for the formation of $Li_3C_3N_3O_3$. The last dissociation constant is estimated as 3.1×10^{-14} (ref. 13) or $\sim 10^{-15}$ (ref. 14). However, Hirt and Schmitt (ref. 14) say: "A third ionic form may exist in the solid state'trisodium cyanurate', [but] it is not observable spectroscopically in [aqueous] solution." Since the reaction of 3 LiOH per mole of cyanuric acid did not give the desired product, a further attempt was made to form the $Li_3C_3N_3O_3$. The autoprotolysis constant of methol might allow the formation of $Li_3C_3N_3O_3$ from $H_3C_3N_3O_3$ and $LiOCH_3$ in methanol. A $LiOCH_3$ solution was obtained from Foote Mineral Company and used in a glove box. Two and three equivalents of $LiOCH_3$ were added to methanolic solutions of cyanuric acid. Since none of the product lithium salts were soluble in methanol, the crystals were digested for 30 minutes under reflux. The crystals were then filtered in air and dried under vacuum. Both samples gave identical IR and NMR spectra, which was also identical to the spectrum of the dilithium salt obtained from aqueous soltuion. The $Li_2HC_3N_3O_3$ product was then refluxed overnight with 10% LiOMe and the product recovered and dried. Although the NMR showed slightly less hydrogen, the product was still primarily $Li_2HC_3N_3O_3$.

Products of DCA-70 reduction were obtained from a lithium amalgam reduction of DCA-70 in methyl formate solution. A green solid was obtained which slowly turned brown in the glove box. This solid had to be separated from mercury by washing in a separatory funnel with hexane.

Infrared spectra of the $LiH_2C_3N_3O_3$, $Li_2HC_3N_3O_3$, and $LiCl_2C_3N_3O_3$ are shown in Figures 36-38. The spectra of cyanuric acid, DCA-70 and the reduction product of DCA-70 at a platinum electrode were discussed previously (Figures 13 and 14). Figures 39 and 40 show the spectra of the Li(Hg) product of DCA-70.

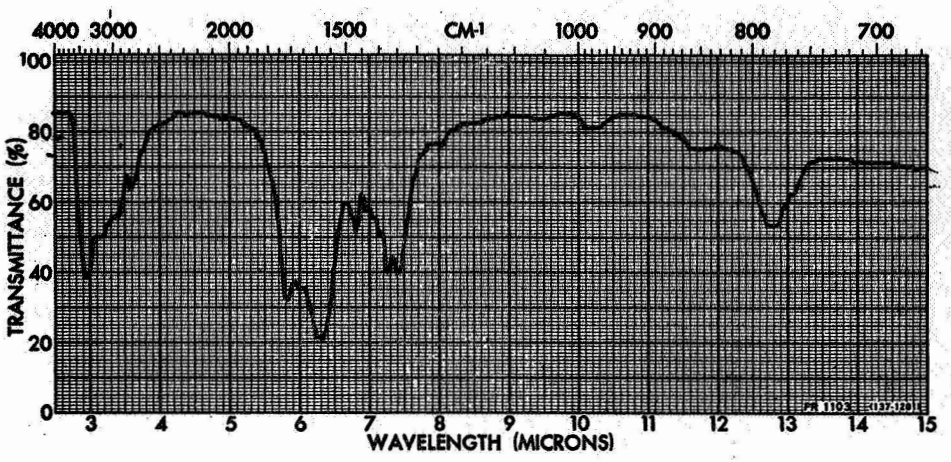


Figure 36. Infrared Spectrum of $LiH_2C_3N_3O_3$

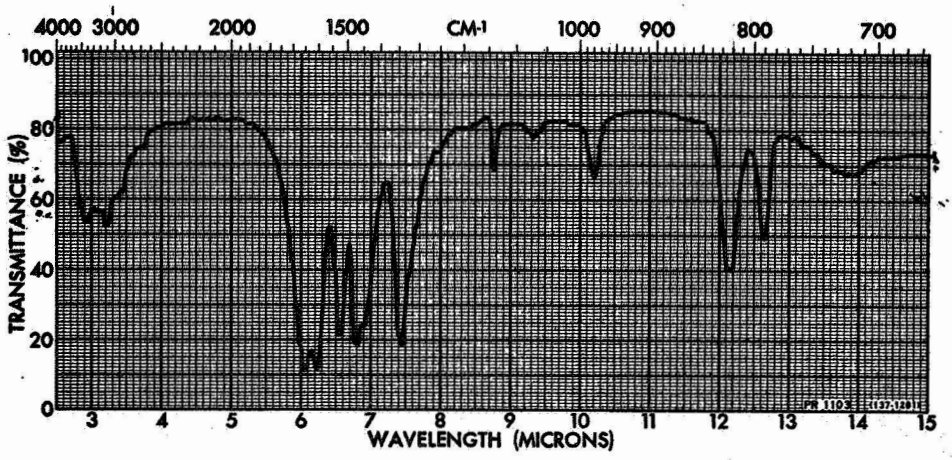


Figure 37. Infrared Spectrum of $Li_2HC_3N_3O_3$

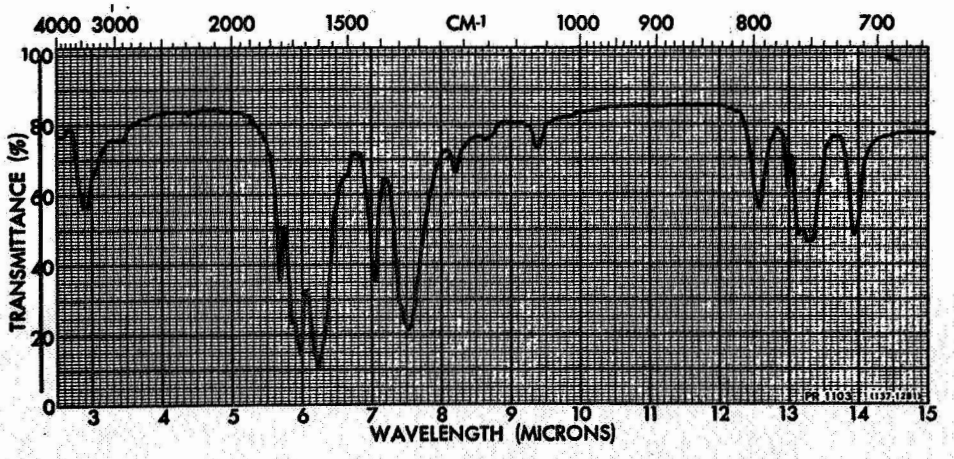


Figure 38. Infrared Spectrum of $LiCl_2C_3N_3O_3$

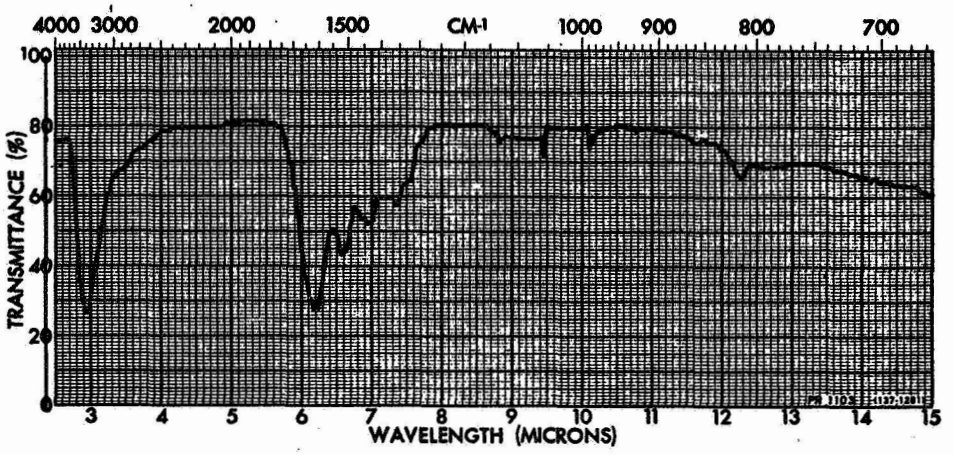


Figure 39. Infrared Spectrum of Li(Hg)/DCA-70 Product

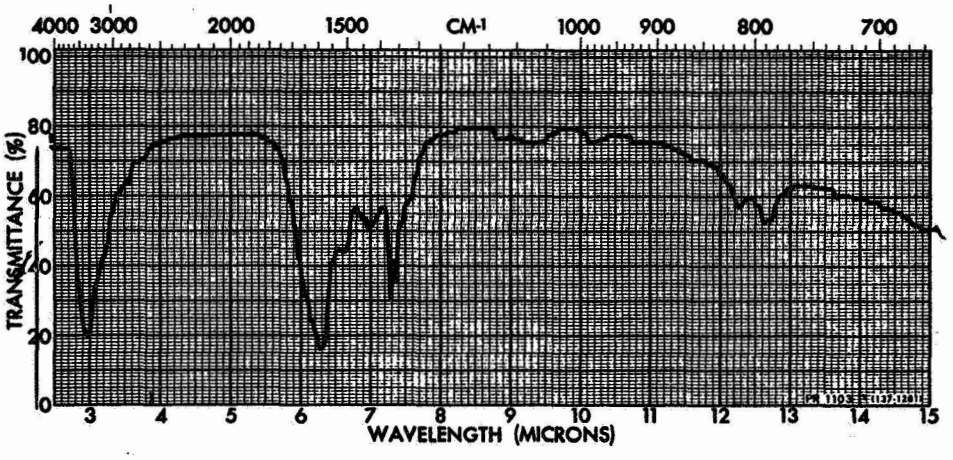


Figure 40. Infrared Spectrum of Li(Hg)/DCA-70 Product After Extraction with MF

Although the purity of this sample is questionable, the product does not correspond to $Li_2HC_3N_3O_3$ or to the DCA-70 reduction product at Pt. Figure 40 is the material in Figure 39 after extraction of LiCl (and other material such as unreacted DCA-70) by Soxhlet extraction with methyl formate for 24 hours*.

The NMR spectra of $Li_2HC_3N_3O_3$ and the Li(Hg) product of DCA-70 showed that the protons of both compounds were exchangeable with D_2O. However, our inability to form $Li_3C_3N_3O_3$ indicates that the acidity of the proton in $Li_2HC_3N_3O_3$ is extremely low. The quantity of protons in the Li(Hg)/DCA-70 product corresponded roughly to the quantity in $Li_2HC_3N_3O_3$; assuming that the solid was $Li_2HC_3N_3O_3$ + 2 LiCl [or the linear polymer $(HC_3N_3O_2)_n$ + 2n LiCl + nLi_2O]. However, the infrared spectrum did not correspond to $Li_2HC_3N_3O_3$ compound, and only a small amount of material was extracted by the Soxhlet process, even though pure LiCl is extracted within the 24 hour period.

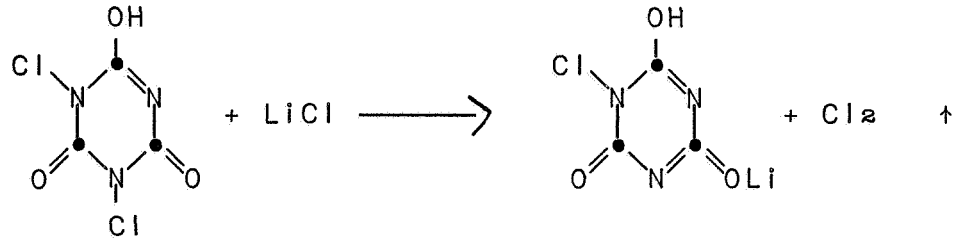
The UV spectra of the lithium salts have been determined in water. The literature (ref. 14) shows that a peak can be found for $HC_3N_3O_3^=$ at pH 10. This peak can presumably be used for analysis of the solubility of cyanuric acid entities in solution. A calibration curve of peak height vs. cyanuric acid concentration was constructed. Samples of $Li_2HC_3N_3O_3$ and Li(Hg) product of DCA-70 were used to saturate methyl formate solutions. An aliquot of saturated solution was taken, evaporated to dryness (since MF interferes with the spectra) and the resulting salt redissolved in water. No $HC_3N_3O_3^=$ entity was observed when the pH was adjusted to pH 10, and addition of $Li_2HC_3N_3O_3$ gave a peak. Hence, the solubility of these products in methyl formate is below the limit of detection, i.e., <0.0025 g/l in these cases.

---

*LiCl does not give infrared absorption peaks and does not alter the spectrum of $Li_2HC_3N_3O_3$. There is evidence that $H_3C_3N_3O_3$ reacts with KBr and changes its spectrum (ref. 15). However, after taking $H_3C_3N_3O_3$ and $Li_2HC_3N_3O_3$ spectra in KBr and Nujol, with and without LiCl, we decided to use KBr. We could see no spectral shift due to LiCl complex formation, even when using Nujol.

c. The Effect of LiCl Production on DCA-70 Stability

During our earlier chronopotentiometric studies (Section II.C), lithium chloride was added to electrolyte solutions in an attempt to approximate the cathode conditions. At that time, it appeared that LiCl caused the evolution of chlorine gas from DCA-70/electrolyte solutions. We conducted several additional experiments to determine whether LiCl might reduce cathode capacity during the discharge period by the following reaction:



(DCA-70)

Since DCA-70 decomposition by this mechanism would probably depend upon the amount of LiCl in solution, a study was made of the solubility of LiCl in MF and in 2M $LiClO_4$-MF solutions. Table 46 shows these solubility data, as well as those for dry $MgCl_2$, which also caused chlorine evolution.

Table 46

THE SOLUBILITY OF LiCl and $MgCl_2$ IN MF AND 2M $LiClO_4$-MF SOLUTIONS

	Solute Solubility (g/l)	
Solvent	LiCl	$MgCl_2$
MF	1.1	0.6
2M $LiClO_4$-MF	6.7	21.8

The decomposition experiments were chosen to approximate those in a discharging cathode. Glass vials with small vent holes were sample holders. DCA-70 samples weighing 0.100 gram were used so the entire sample could be titrated at the end of the experiment. Decomposition at the end of 6 hours was measured. The amount of LiCl added equaled the amount that would be produced from 0.100 gram of DCA-70 half-way through a 6 hour discharge. The amount of $MgCl_2$ added was equivalent in chloride

concentration to that of the LiCl additive (or 0.5 molar amount of LiCl). $MgCl_2$ was tested since it was more soluble in electrolyte than LiCl, and the DCA-70 decomposition might be assumed to be proportional to the chloride ion concentration in solution. When Shawinigan Acetylene Black (SAB) was added, it was in the same proportion found in our cathode.

The data are shown in Table 47. The ACL number of an active halogen compound is based on the oxidative capacity (amp-min/g) of the compound relative to chlorine, which is assigned a value of 100. Therefore, DCA-70 has an ACL-number of 70 and 70 percent of the capacity of Cl_2. The ACL number is determined by the iodide-thiosulfate technique (ref. 1).

Experiments were carried out at two concentrations - 5.0 ml and 0.1 ml of solution per 0.100 gram of DCA-70. The latter concentration is characteristic of that in a discharging cathode, while the larger amount of solution (5.0 ml) should intensify any decomposition noted with the smaller amount of solvent (0.1 ml).

The data show that chloride containing salts increase the rate of DCA-70 decomposition. The more soluble the solute, the larger the decomposition. A direct proportionality is not observed, however, (see $MgCl_2$ in $LiClO_4$-MF) probably because the equilibrium

$$MgCl_2 \rightleftharpoons Mg^{+2} + 2Cl^-$$

lies far to the left. The presence of SAB appears to reduce DCA-70 decomposition, possibly by adsorption of any Cl_2 produced.

d. Identification of DCA-60 as an Impurity in DCA-70

Soxhlet extraction experiments were carried out on various known cathode components prior to attempts to separate and identify the unknown products present in our discharged cathode.

Extraction of DCA-70 with MF left an insoluble residue which equaled 10 percent of the sample, and gave an ACL number of 59 to 60. This residue had been noted earlier (Table 6), but it was thought at that time that it might be a less soluble crystal form of DCA-70, or a charge-transfer complex between DCA-70 and a small amount of cyanuric acid.

Table 47

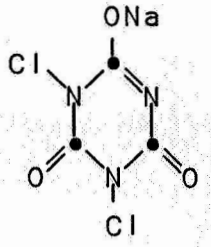
EFFECT OF CHLORIDE ON DCA-70 STABILITY
(0.100 g DCA-70 in MF or 2M $LiClO_4$-MF, 6 hr, 0.021 g LiCl or 0.024 g $MgCl_2$ ADDED)

Solute	Solvent Amount (ml)	DCA-Number $LiClO_4$-MF	DCA-Number MF
None[1]	-	70	ND[2]
None	5.0	66	66
LiCl	5.0	60,55	64,58
$MgCl_2$	5.0	56,49	62,62
$MgCl_2$[3]	5.0	54	ND
None	0.1	69	ND
LiCl	0.1	64	ND
$MgCl_2$	0.1	61	ND
$MgCl_2$	0.1	67	ND

(1) No 6 hr. stand. Titrated immediately.
(2) Not determined.
(3) 0.02 g SAB

A 110 gram sample of DCA-70 was magnetically stirred in 1100 milliliters of methyl formate for 5 minutes. The insoluble portion was filtered and dried at 60°C/15 torr to give 9.6 grams (8.7%) of white crystalline solid with an ACL-number of 59.5. The MF filtrate was evaporated to yield 94.1 grams (85.5%) of DCA-70 with an ACL-number of 70.5.

Flame tests showed the insoluble fraction to be a sodium salt. This was confirmed by elemental analysis which showed 7.09 percent sodium by activation analysis. These data best fit the sodium salt of DCA-70 which is sodium dichloroisocyanurate (DCA-60).



(DCA-60)

Electrochemical data concerning the performance of the two DCA fractions are found in Section II.D.1 of this report.

3. Gas Evolution Experiments

a. Gas Analysis

Work on another project showed that a cell, which was more vapor tight than our research cell (ref. 1), could be constructed from a 20mm x 62mm cylindrical glass vial containing a number 3 rubber stopper. The tighter nature of this new cell allowed the observation that gas was evolved from the Li/DCA-70 cell after the addition of electrolyte to the active components. We felt that this phase of the Li/DCA-70 study was important enough to pursue further, and a quantitative analysis of the gaseous products was carried out.

The gases evolved were collected in a mercury displacement system (Figure 41). Gases were collected at open circuit, during discharge, and after discharge. The data, determined on 1.5 amp-hr cells, are shown in Table 48 and can be summarized as follows:

- Lithium and purified MF (4A molecular sieve treatment) generates very little gas [0.9 ml after 2 hr, (cell 105044)].
- Lithium and purified electrolyte ($LiClO_4$-purified MF) gives slightly more gas [2.2 ml after 1.5 hr, (105040a)] than is generated with purified MF alone.

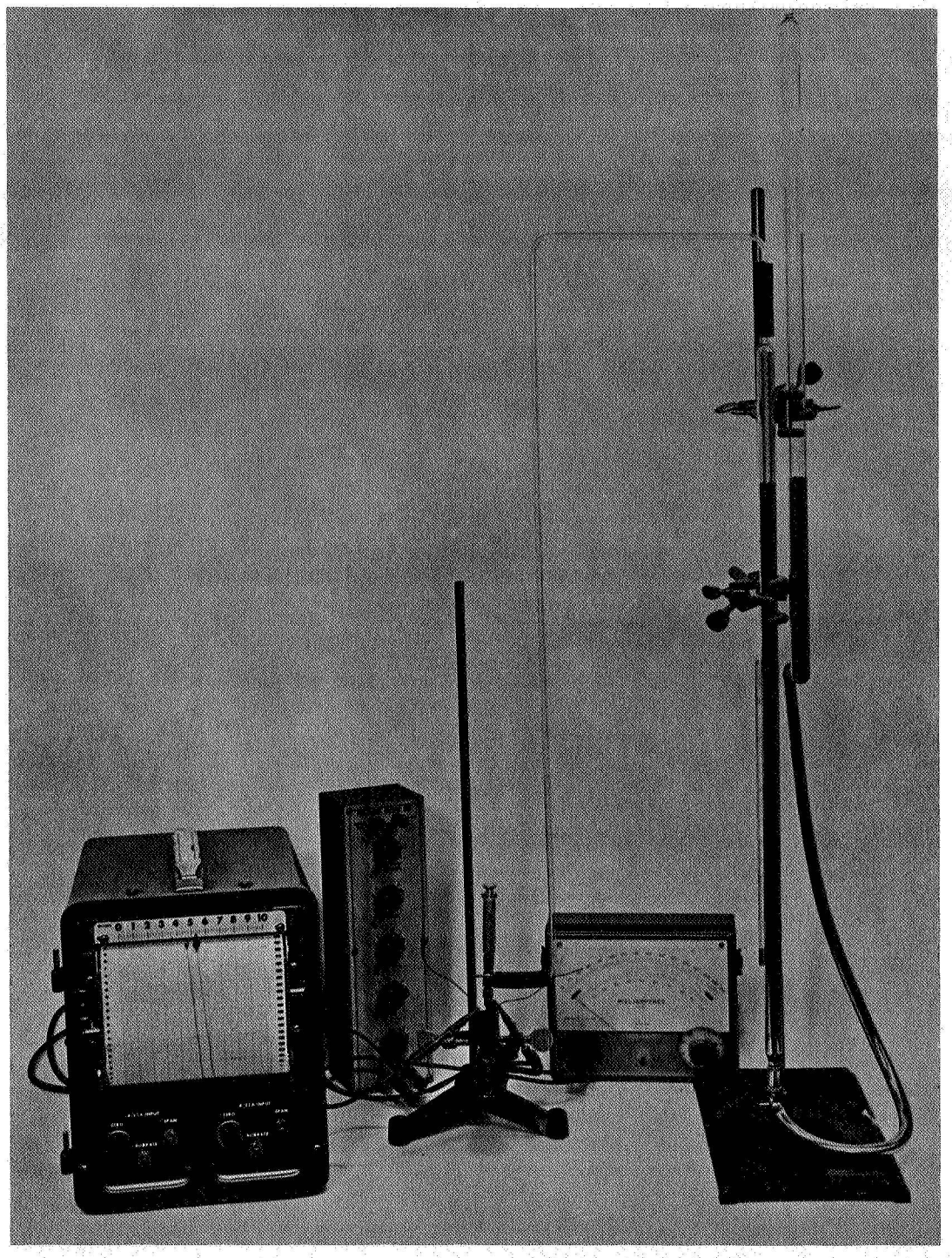


Figure 41. Apparatus for the Measurement of Cell Gassing During Discharge.

Table 48

GAS EVOLUTION FROM Li/2M $LiClO_4$-MF/DCA-70 CELLS
[1.57 amp-hr capacity, discharged at 10 ohms (3 hr rate)]
(Temperature 21-22°C, Barometric Pressure 763-777 torr)

System	Cell Number (1050--)	Gas Evolution in ml (time in min) O.C.[1]	During Run	After Run	at 60 min.	Fraction of Sampling Bulb Filled	Gas Analysis by VPC (torr) MF	H_2	CO	CH_4	Gas Analysis as Percentage of Total(%) MF	H_2	CO	CH_4	(IR) CO_2	Electrical Characteristics (100 load) Cathode Efficiency (%)	Energy Density (w-hr/lb)
Full Cell*	38	6.7(5)	10(170)	57(960)	15.0											56.5	120.7
Full Cell†	39	7.7(5)	30(203)		24.4											56.8	129.1
Li/($LiClO_4$-MF)*	40a	2.2(95)			1.8												
Li/($LiClO_4$-MF)†	40b	24(167)			8.2	24/320	26	26	<1	2	45	45	<2	3.5			
Full Cell*	41	57(60)	8.7(45)[2]		57.1	57/187	132	52	<1	<1	57	22	<0.5	<0.5		55.0	125.2
				48.3(420)		33/320	25	50	5	5	32	65	6.5	6.5	5		
Full Cell* without Li	42a	5.5(960)			0.7	5.5/250	12	0	0	0	79	0	0	0			
Full Cell* without DCA-70	42b	5.5(143)			2.8												
Full Cell*(3)	43	59.5(60)			59.5	59/320	113	53	<1	<1	81	38	<1	<1			
Li/MF*	44	0.9(136)			0.4												
Full Cell†	45	70(60)			70	90/187	208	90	2	<1	73	32	0.7	<0.5	12		
			30.6(202)			30.6/320	78	30	1	5	107	41	1.3	6.9	8	58.1	127.0
				15.2(900)		15.2/250	31	10	<1	4	67	22	<2	8.7	~3		

(1) Open circuit gas volume is the total gas evolved for cells not discharged.
(2) Gas collected at 45 min - cell ran longer.
(3) Cell not discharged. 5.8% DCA-70 loss during 1 hr open circuit wet-stand (thiosulfate titration).

* Purified electrolyte (4A molecular sieve treatment of MF)
† Standard electrolyte

- Lithium and standard electrolyte ($LiClO_4$-MF not treated with sieves) gave ten times as much gas [24 ml in 2.5 hr, (105040b)] as when purified electrolyte was used.

- A full cell without the Li anode generates little gas [5.5 ml in 16 hr (105042a)].

- A full cell without the DCA-70 depolarizer generates little gas [5.5 ml in 2.5 hr, (105042b)].

- A full cell using purified electrolyte (5 minute wet-stand) generates less than 20 ml of gas when discharged at the 3 hour rate (105038).

- Discharge (after a 1 hr wet-stand) of a cell using standard electrolyte gave about the same volume of gas (100 ml) as the volume obtained using purified electrolyte (105045 and 105041). The amounts at open circuit, during discharge and after discharge were somewhat different, however, as was the gas composition.

The quantity of gas evolved from a 1.5 amp-hr Li/$LiClO_4$-MF/DCA-70 cell using excess electrolyte [55% excess relative to the amount used in our research cell (ref. 1)] varies with how the cell is discharged. If the cell is discharged with a minimum wet-stand time, 15 to 20 milliliters of gas evolution is obtained after discharge at the 3 hour rate.

If the cell stands at open circuit for 1 hour, is discharged at the 3 hour rate, and then is allowed to stand under load for an additional 10 hour period, approximately 100 ml of gas is generated.

Gas formation was initiated by the addition of electrolyte to an evacuated cell. The gases generated by the cell were removed from the mercury displacement system by means of evacuated glass bulbs of known volumes. The bulb pressure was equilibrated to 1 atmosphere by addition of air. Preliminary infrared spectroscopic examination of the gases indicated that methyl formate, carbon dioxide, carbon monoxide and methane were major components. A vapor phase chromatographic (vpc) technique was developed (3 ft. Poropak 50/80 mesh, 150°C, 15 psi He, 1 ml sample) for the quantitative determination of methyl formate in the gas sample. A second vpc technique was developed for H_2, CO and CH_4 (12 ft. 13X molecular sieves 40/60 mesh, 44°C, 15 psi He, 1 ml samples). Vpc analyses were made on a Perkin-Elmer Model 154 Vapor Fractometer. The instrument was calibrated with standard gas samples,

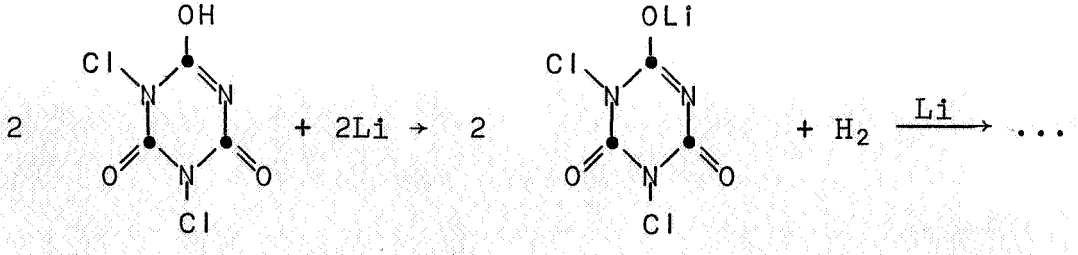
and the quantity of each gas in the sample from the cell was determined in units of torr (mm of Hg). A sample chromatogram is given in Figure 42. The gas pressure was converted to gas volume in milliliters by the ratio of gas pressure ÷ 760 torr. The percentage of each gas in the sample was determined by dividing the individual gas volumes by the total gas volume collected in the mercury displacement system. Carbon dioxide could not be determined by the vpc analysis. An estimation of the CO_2 content using infrared spectroscopy (absorption at 2300 cm^{-1} vs standard samples) gave approximate CO_2 pressures.

As seen in Table 48, most of the gas present is made up of two components - methyl formate and hydrogen. It is also noted that the total percentage is greater than 100 percent in some analyses. This is due to high methyl formate values. It appears that the hydrogen evolved carries MF with it out of the cell. Part of the MF then condenses in the glass tube leading from the cell to the mercury displacement system (experimentally observed). While this condensed MF does not appreciably increase the gas volume in the Hg system, it is evaporated into the evacuated gas sampling bulb, because of its low boiling point (31°C). The vapor pressure of MF at 20°C is 476 torr (ref. 16). The vapor pressure of our electrolyte (2M $LiClO_4$-MF)is presently unknown, but is somewhat lower than that for pure MF. The percentage of MF in the gas sample should be constant [(100%) (vap. press. electrolyte ÷ 760 torr)] for all runs. While the quantitative MF data is too high, the percentage assigned to H_2, CO, and CH_4 are correct since their concentrations are based on direct vpc measurements and are not related to the MF determination.

b. Origin of Gas Evolution

(1) Chemical Possibilities

The data from Table 48 indicate that both Li and DCA-70 must be present to obtain a significant amount of cell gassing (cells 105041, 42a, 42b). It is likely, therefore, therefore, that the gassing is due to self-discharge. A logical hydrogen producing, self-discharge reaction is shown in the following equation:



DCA-70

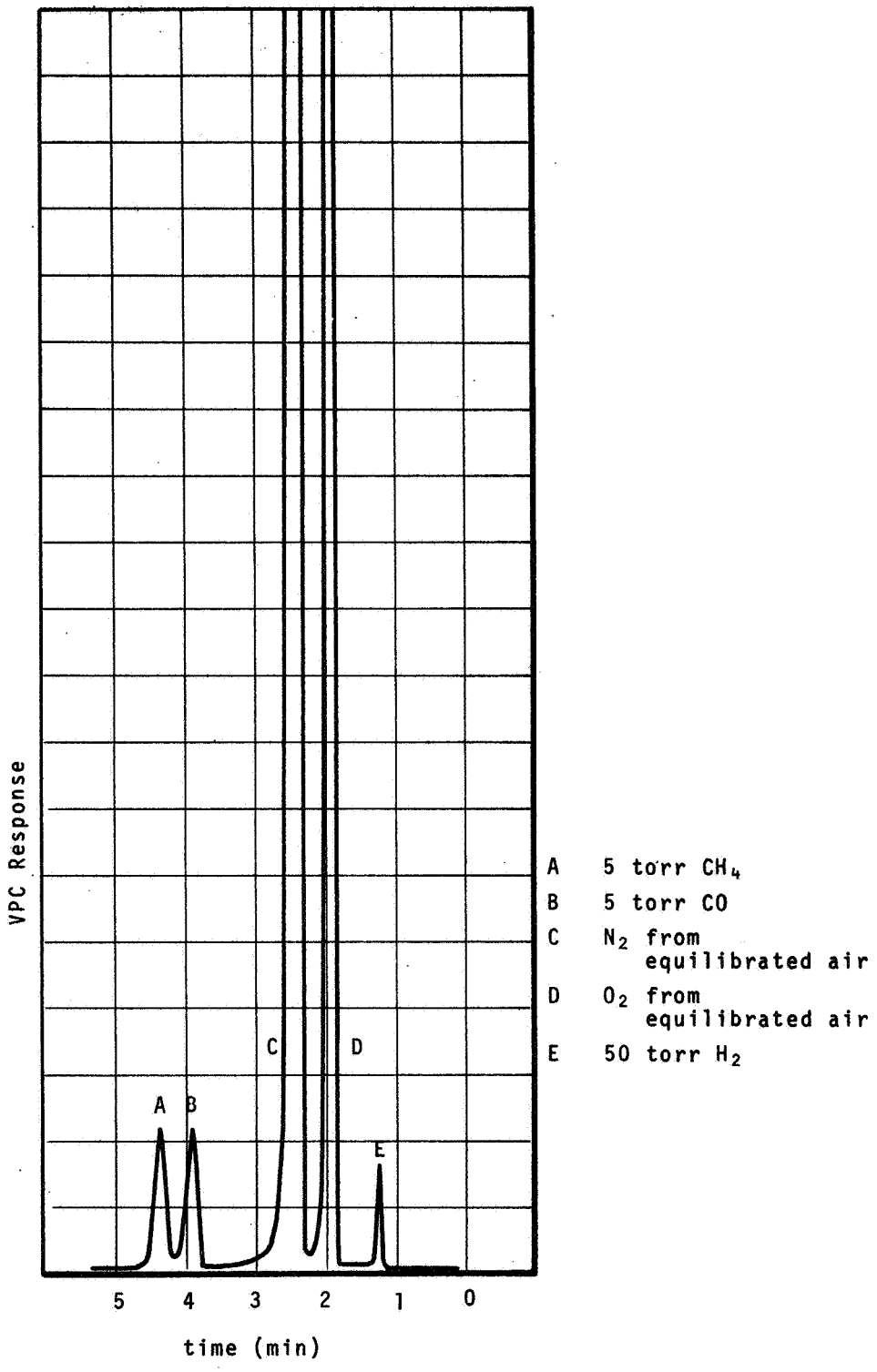
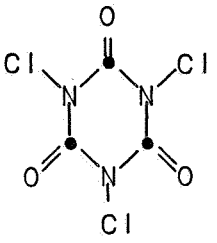


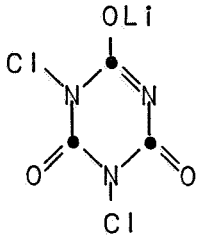
Figure 42. Vapor Phase Chromatogram of Gaseous Discharge Products.

It can be calculated from run 105043 that a 5.8% DCA-70 loss by this reaction would yield 10.6 ml of H_2 at 22°/760 torr. This corresponds to the 22.4 ml found experimentally. The correspondence might be even better if the theoretical amount of H_2 produced was based on some measure of DCA-70 proton loss, rather than the 5.8% active chlorine loss actually measured.

If this reaction was the source of hydrogen in DCA-70 cells, then the use of trichloroisocyanuric acid (TCA-85) or the lithium salt of DCA-70 ($LiCl_2CYA$), neither of which contain protons, should solve the majority of the gassing problem.



(TCA-85)



($LiCl_2CYA$)

The electrochemical cells were therefore constructed with the TCA-85 and $LiCl_2CYA$ as replacements for DCA-70. Gassing data was taken as a function of time, and is presented in Table 49. It is seen that , in both cases, the gassing is comparable to that from DCA-70. This indicates that the gas evolution is not due primarily to an acidic hydrogen, but rather may be due to an impurity in the chlorinated cyanuric acids; for example, water.

Both the TCA-85 and the $LiCl_2CYA$ were redried by our standard method (vacuum drying over P_2O_5). Since neither compound should contain hydrogen, they were analyzed by NMR spectroscopy. No protons were found in the TCA-85 sample as analyzed by this method. The $LiCl_2CYA$, however, contained the equivalent of $\sim$2% water. These data indicate that gas evolution is not a function of impurity concentration (e.g., water), since TCA-85, which contained no protons by NMR analysis, produced as much gas as DCA-70. It is possible that the gasses produced from the reaction of Li and TCA-85 or $LiCl_2CYA$ are not the same as the gas (hydrogen) produced from Li and DCA-70. No analysis, other than gas volume, was made on the products of the former reactions. If chlorine or hydrogen chloride were produced from the TCA-85 or $LiCl_2CYA$ reactions with lithium, this would explain gas evolution without acidic protons being present. However, neither gas was observed, visually, when gas samples were removed from the collection apparatus. The possibility that nitrogen or NCl_3 is produced by ring degradation still exists.

Table 49

GAS EVOLUTION WITH PROTONIC AND NON-PROTONIC DEPOLARIZERS

(Discharge through 20 ohms)

	Gas Evolved (ml)		
Depolarizer	After 60 min	Total	Cell
DCA-70	40	51	105070
$LiCl_2CYA$	65	65	105071
	63	68	105072
TCA-85	54	>80	105073

It does not appear that the amount of gas produced is related to depolarizer solubility (Table 32).

In an attempt to measure gas evolution from the self-discharge reaction, 1 cm^2 of lithium ribbon was added to a 1% solution of DCA-70 in 2M $LiClO_4$-MF. No significant gas evolution was obtained. Higher DCA-70 concentrations were not studied due to possible safety hazards.

(2) Electrolytic Studies

Another possible source of gas evolution was electrochemical. It was possible that the active chlorine compounds reacted with the electrolyte to form a product which was converted to a gas at the anode*. The question of whether this product was formed at carbon polarized to 4 volts vs Li, or was due to a chemical reaction of DCA-70 and MF was answered by polarizing a Li/C cell (without DCA-70).

A gas-tight cell of Li/$LiClO_4$(MF)/Carbon was set up similar to the normal cell, but without DCA-70. At open circuit, 1 ml of gas was collected and the potential was 1.4 volts (electrometer reading). However, 90 mA (2mA/cm^2) was required to reach 3.5 volts. At this point the cell was warm and further current increase was not practical.

A gas sample was obtained at this time (30 ml in 1 hour). The sample was analyzed as 16 torr H_2 pressure, 3 torr CH_4 and 4 torr CO. It is impossible that the cell would require this amount of current to reach even 3.5 volts. This would severely limit the Li/DCA-70 cell, since the corrosion current would be much greater than 6 mA/cm^2 at 4.0 volts. However, the gas sample data is not unlike the data collected for full cells (Table 48).

It was felt that the electrolyte might be impure. Thus, new electrolyte was prepared and the test repeated. This time $\sim$1 mA/cm^2 was required to bring the voltage from 1.95 V to 3.85 volts in 20 minutes. At this point the voltage decreased to 3.70 volts. Increasing the current to $\sim$2 mA/cm^2 increased the voltage temporarily. Only 6 ml of gas was collected in 1-1/2 hours, in this experiment. This was an insufficient quantity for analysis.

* The C/DCA-70 electrode did not produce gas, hence an anode is necessary for gas evolution.

Discharge data was collected on each electrolyte and no significant difference was found. Therefore, DCA-70 apparently deactivates the carbon, allowing 4.0 volts to be reached without significant electrolysis. The primary gassing is apparently not due to electrolysis of the solvent and concommitant reaction with lithium, although with impure electrolyte this cannot be ruled out. Finally, electrolyte purity is critical in this gassing and electrolysis analysis.

c. The Effect of Electrolyte Salt and Low Temperature on Cell Gassing

The effect of $LiClO_4$ purity was studied with a sample from Atomergic Chemetals used as the electrolyte salt. The $LiClO_4$ sample was similar to that produced for Rocketdyne, which was well characterized (Contract NAS3-8521). While the gas measuring system inadvertantly was not connected to the cell for the first two minutes after addition of the electrolyte, the data in Figure 43 (see also Table 50) show no appreciable decrease in gas evolution due to a change of $LiClO_4$ source.

Results of a low temperature test (109286) are also described in Table 50. This cell was immersed in a toluene bath, which in turn was cooled by an ice-water bath. The toluene temperature varied from 3-5°C. Upon addition of ambient electrolyte, there was an immediate evolution of gas (26 ml); the quantity decreased to 15 ml as the cell returned to 4°C. The increase in gas volume after the initial surge was slight (6 ml in 2 hours). Furthermore, much of the gas was methyl formate, since cooling the gas burette with a small piece of dry ice decreased the gas volume by 5 milliliters.

Excess methyl formate was also observed in the bottom of the cell in the 4°C test. This is not seen at ambient conditions, and indicates that extra electrolyte is normally used in vaporization cooling. The discharge of the cell at 4°C at 20 ohms (approx. 6-hour rate) yielded 56.8% cathode efficiency and 134 w-hr/lb. By warming the cell to room temperature when the voltage reached 2.0 V, an additional 7.5% in efficiency and 15 w-hr/lb in energy density were obtained.

Thus, gassing can be reduced by low temperature operation, and much of the gas produced is methyl formate vapor, which is readily condensible under pressure.

Further low temperature tests were made to compare gassing differences between $LiClO_4$ and $LiAsF_6$ electrolyte salts. These tests are described in Table 51.

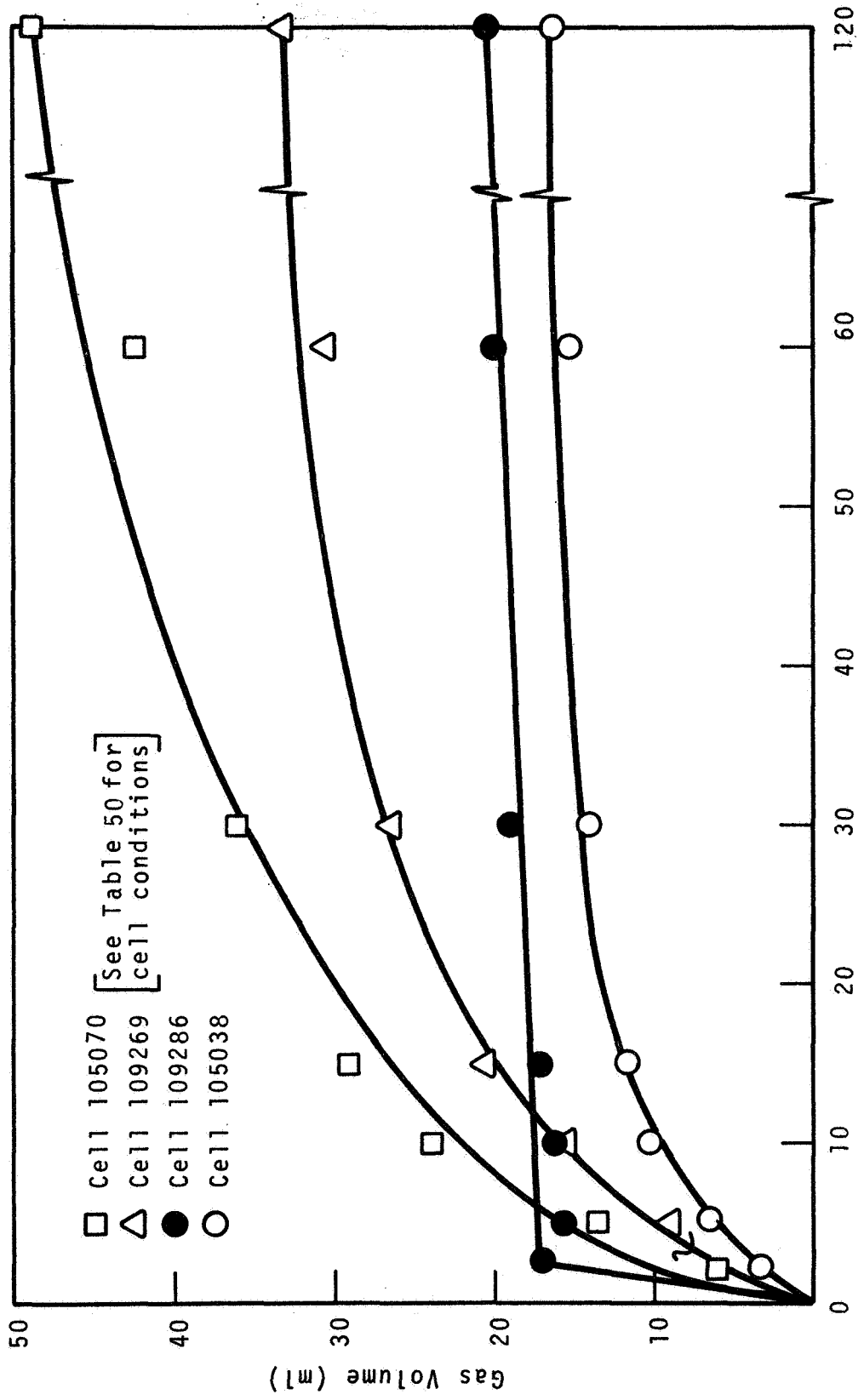


Figure 43. Gas Evolution in Li/DCA-70 Cells

Table 50

GAS EVOLUTION IN Li/DCA-70 CELLS

Type of $LiClO_4$	Cell No.	Temp. (°C)	Resistance (ohm)	Efficiency (%)	Energy Density (w-hr/lb)
Standard	105038	22	10	56.5	121
Standard	105070	23	20	64.5	161
Purified†	109269	22	20	56.4	127
Purified	109286	4	20	56.8	134
Purified	109286	Amb.*	20	64.3	159

*After reaching 2.0 volts at 4°C, the cell was allowed to warm to ambient conditions

†Obtained from Atomergic, Inc. (see text)

Table 51

GASSING AND PERFORMANCE OF Li/DCA-70 CELLS
AT LOW TEMPERATURE (4°C)
(Discharge through 20Ω)

Cell No.	Electrolyte	Temp °C	Time (min)	Gas Vol. (ml)	Efficiency (%)	Energy Density (w-hr/lb)	Average Voltage (volts)
110729	4.25 ml 2M	25	10	39			
	$LiAsF_6$		60	54			
			160	55	23.5	47	2.73
105070	4.25 ml 2M	23	10	24			
	$LiClO_4$		60	40			
			374	52	64.5	161	3.30
110732	4.0 ml 2M	4	10	-2.2			
	$LiAsF_6$	4	60	-1.4			
		4	295	-1.3	46.2	106	2.88
	+0.5 ml*	amb[τ]	381	-1.1	58.0	119	2.78
110739	3.5 ml 2M	4	10	14.3			
	$LiClO_4$	4	60	23.2			
		4	267	23.2	44.0	111	3.06
		amb	342	25.9	53.5	128	2.90
	+0.5 ml	amb	431		66.7	148	2.87

* Electrolyte addition was at 4°C and did not improve cell performance.

[τ] Temperature of cell raised to ambient.

In the test of $LiAsF_6$ at ambient temperature, there was no improvement in cell gassing over the $LiClO_4$ test. However, the ambient temperature for the $LiAsF_6$ run was 25°C versus 23°C for the $LiClO_4$ test. At 4°C, the gassing of the $LiAsF_6$ cell was negligible. The cell is activated after being evacuated; hence, the negative pressure is explainable. The total gassing of this cell (ca. 1 amp-hr delivered) is 2-3 cm^3 (STP). The major gassing of the $LiAsF_6$ cell is presumably due to methyl formate vaporization and the partial pressure of MF in the dead space of the cell and gas measuring apparatus. A test with $LiClO_4$ at 4°C, however, showed considerable gassing. Again, the electrochemical performance of the $LiClO_4$ cells surpassed that of the $LiAsF_6$ cells (see Section II.D.1).

The solubility of DCA-70 was measured in 2M $LiAsF_6$. The electrolyte salt was found to decrease the DCA-70 solubility. Thus, the solubility of DCA-70 in MF is 15 wt-%, and in 2M $LiAsF_6$ it is 7 wt-%. This may be the reason for the better performance of $LiClO_4$ electrolyte cells, since the solubility of DCA-70 in 2M $LiClO_4$ is 12 wt-%, and the rate of solubility is also much higher than in 2M $LiAsF_6$.

4. Cell Protection Experiments

a. Introduction

The Li/DCA-70 Dry Tape system may require a method for protecting the tape from atmospheric contact. This method could be the enclosure of the entire system, or the protection of only those elements requiring protection. While it was known that lithium must be protected from water vapor, nitrogen and oxygen, the long term effect of water vapor on the cathode was unknown. Water might lower the DCA-70 stability, thus decreasing cell efficiency, and it could also cause cell gassing. A program was initiated to evaluate the necessity for cathode protection, and the possibility of protecting the entire tape in a polymer envelope.

If the cathode did not need protection, then anode protection might be achieved with polymer envelopes or films. Anode protection methods such as salt complexing or metal alloying to effect passivation were not studied.

The program was divided into two major parts - one involving various lithium coating methods and the other total cell encapsulation. Complete data can be found in Appendix Tables A-7 to A-9.

b. Lithium Coating

The preferred polymer coating for lithium would be a plastic which is soluble in methyl formate which upon solution, would not greatly increase the viscosity or decrease the conductivity of the electrolyte. Methyl methacrylate is soluble in MF, relatively impermeable to water vapor and was readily deposited as a film on lithium from a benzene solution. Three lithium strips were protected with various thicknesses of polymer, and left at ambient conditions. Each coating started to peel away after 1-3 days, leaving unprotected lithium. A thin film afforded better protection than a thick film. No method of correcting the peeling was obvious. There is most probably, a chemical reaction between lithium and the polymethylmethacrylate.

Paraffin coating of Li was attempted from solvents and from the melt. Only the melt gave a non-crystalline coating. The coating from molten wax gave a protection which appeared to last for at least a month. Therefore, a series of tests were set up to study discharge of lithium versus new cathodes after 1 week and 1 month periods. The wax must be removed by a separate solvent wash, (e.g., ligroin) just prior to use.

Lithium strips (1 x 4 inches) were dipped in molten paraffin wax, in a glove box. The increased weight (0.2 gram) corresponds to a paraffin thickness of 0.002 inch. These samples were placed in storage at ambient and 70°F, 50% R.H., and removed after 1 and 4 week periods. The paraffin wax was removed with hexane in the glove box, before assembling the test cell for discharge. The increased weight due to paraffin protection is 0.004 g/cm^2 of tape.

Data on cell discharge, using this lithium and new cathodes, are shown in Table 52. Table 53 can be used as a basis for comparison with new lithium. The protection for one week periods is very good.

Only one of the four week wax-protected samples of lithium could be discharged effectively. The lithium was brittle in all cases, and in one instance, the tab was almost completely disconnected before the cell was assembled. As would be expected, the lithium surface was grey and at the start of the discharge and the voltage was low. During discharge, however, the lithium became etched and the cell performance improved.

Table 52

DISCHARGE OF PARAFFIN-PROTECTED LITHIUM

(Discharge at 10 mA/cm^2 vs New Cathodes)

Cell	Storage Time (weeks)	Average Voltage (V)	Efficiency (%)	Energy Density (w-hr/lb)
		Ambient Conditions		
109273	1	2.99	56.3	144
109274	1	3.23	55.0	155
		70°F, 50% Relative Humidity		
109278	1	3.14	42.4	115
109279	1	3.13	48.9	132

Table 52 (Continued)

DISCHARGE OF PARAFFIN-PROTECTED LITHIUM

(Discharge at 10 mA/cm^2 vs New Cathodes)

Cell	Storage Time (weeks)	Average Voltage (v)	Efficiency (%)	Energy Density (w-hr/lb)
		Ambient Conditions		
110702	4	3.07	51	136
110703	4	~2.3	2	3
		70°F, 50% Relative Humidity		
110706-1	4	2.87	7	8
110706-2	4	-	0	0

Table 53

DATA ON TAPES DISCHARGED IMMEDIATELY

(Discharge at 10 mA/cm^2, 1.5 ml electrolyte,
Cathode 17% carbon, 1 hr P-K blend)

Cell	Average Voltage (V)	Cathode Efficiency (%)	Energy Density (w-hr/lb)
109238	3.15	56.2	152
109291	2.87	52.2	138
109295	3.14	53.9	156
Ave. values	3.05	54.1	149

One lithium strip was left unprotected at ambient conditions (72°F, 20% rel. humidity) for six hours before discharge. The lithium became severely corroded. However, under the standard discharge conditions (10 mA/cm^2) the cell gave an average of 2.79 volts, 32% cathode efficiency, and 82 watt-hr/lb (Cell No. 110701).

c. Tape Encapsulation

(1) Polymer Screening Experiments

Three films were chosen for initial study. These were:

Polymer	Thickness
Saran	0.0005 inch and 0.002 inch
Aclar 33C	0.002 inch
Polyethylene	0.005 inch

Both lithium and complete cells were packaged with these materials. After one week under ambient conditions, the Aclar film was obviously superior. These data agree with earlier data on electrolyte encapsulation concerning polymer-moisture permeability (ref. 1). Figure 44 shows the encapsulated cells.

The following experimental program was set up with Aclar film encapsulation:

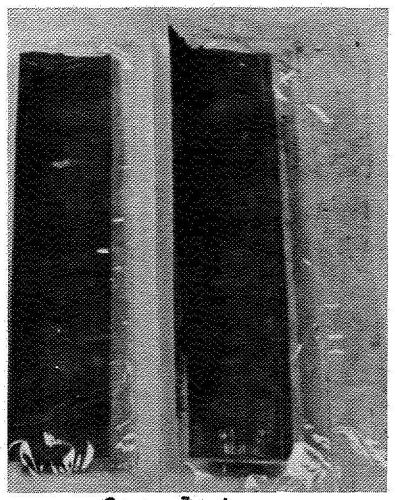
I. Ambient Conditions - Tests after 1 week, 1 month, 3 months
   A. Total cell encapsulation - duplicate tests, 10 mA/cm^2
   B. Lithium encapsulation - single test, 10 mA/cm^2
      1. Li vs cathode stored same time
      2. Li vs new cathode

II. 70°F and 50% Relative Humidity - same series as above

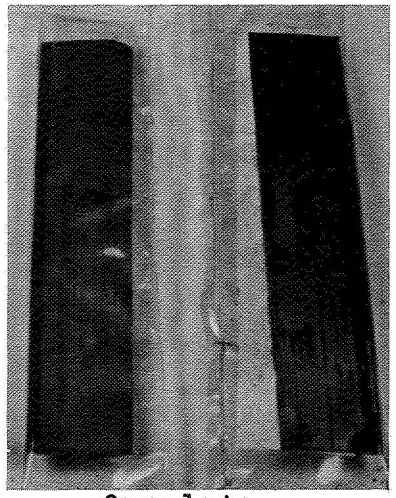
A Blue M Constant Temperature/Constant Humidity Cabinet was used for the controlled temperature and humidity experiments. The cathodes were prepared from the 1 hour P-K blender mix.

The Aclar envelope was 0.002 inch thick and added 0.95 gram to the weight of the anode or to the cell. The cell weight was 3.87 grams. This envelope, however, must also cover a 1-inch lithium tab. Hence, the Aclar weight is 0.018 g/cm^2 of tape.

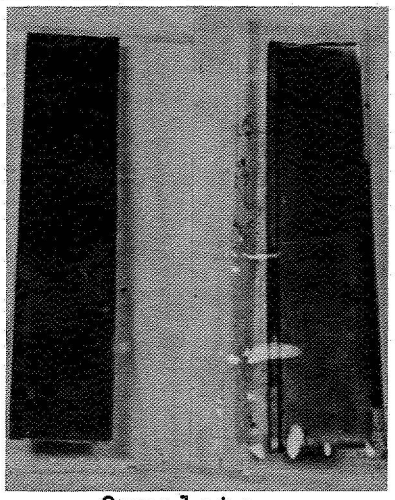
Immediately After Encapsulation



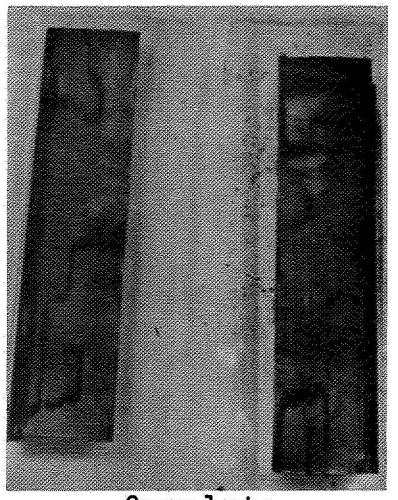
Complete
Lithium Cell
Saran 0.0005"



Complete
Lithium Cell
Saran 0.002"

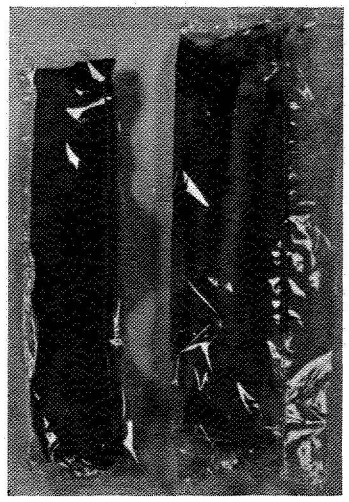


Complete
Lithium Cell
Aclar 33C 0.002"

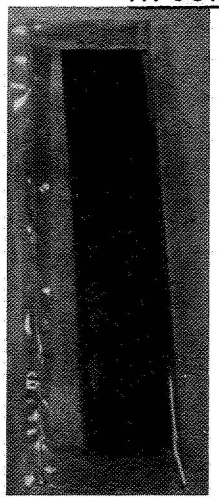


Complete
Lithium Cell
Polyethylene 0.005"

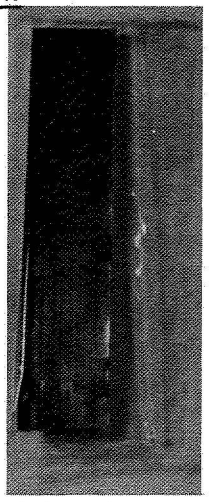
After 1 Month



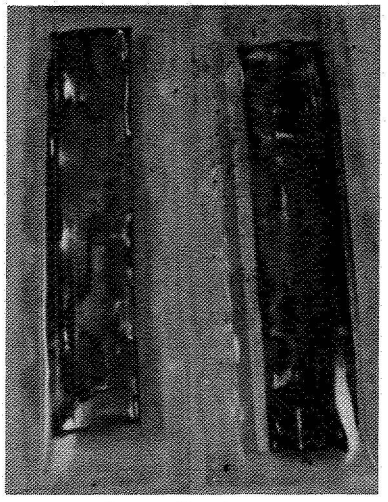
Complete
Lithium Cell
Saran 0.0005"



Complete
Cell
Saran 0.002"



Lithium
Aclar 33C 0.002"



Complete
Lithium Cell
Polyethylene

Figure 44. Dry Tape Protection by Polymer Encapsulation

(2) Results

Discharge data for 1, 4 and 12 week storage periods are shown in Table 54. Total cell encapsulation was completely effective in protecting cells for three month periods.

Results were the same when protected lithium was discharged against either new cathodes or protected cathodes. There is no evidence of chlorine vapor from DCA-70 reacting with the lithium during the storage period in Aclar. However, cathodes left unprotected under the same conditions were significantly degraded. The cathode left at 50% relative humidity lost 31% of its active chlorine content and required an extra 0.5 ml of electrolyte for activation. The performance was 2 to 3 times worse than that expected of a new cathode. The apparent low energy density of the ambient cathode cell (No. 110737) is due to the light weight of this sample. The efficiency and voltage are normal.

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Table 54

DATA ON ACLAR-PROTECTED SAMPLES STORED UNDER VARIOUS CONDITIONS
(Discharge at 10 mA/cm^2, Cathode is 17% carbon, 1 hr P-K blend)

Ambient, Total Cell Encapsulation

Cell	Storage Time (weeks)	Average Voltage (V)	Efficiency (%)	Energy Density (w-hr/lb)
109243	1	3.07	61.6	149
109277	1	3.09	58.5	157
109283	4	3.14	61.7	162
109284	4	3.09	55.9	147

Ambient, Lithium Encapsulation

Cell	Storage Time (weeks)		Average Voltage (V)	Cathode Efficiency (%)	Energy Density (w-hr/lb)
	Li (Aclar Protected)	Cathode (Unprotected)			
109275	1	1	3.09	59.8	159
109285	4	0	3.13	55.8	150
110702	4	4	3.14	58.1	158

70°F, 50% Relative Humidity, Total Cell Encapsulation

Cell	Storage Time (weeks)	Average Voltage (V)	Efficiency (%)	Energy Density (w-hr/lb)
109271	1	3.10	59.4	158
109272	1	3.03	54.6	143
109298	4	3.12	57.7	149
109299	4	2.96	60.4	146

70°F, 50% Relative Humidity, Lithium Encapsulation

Cell	Storage Time (weeks)		Average Voltage (V)	Cathode Efficiency (%)	Energy Density (w-hr/lb)
	Li (Aclar Protected)	Cathode (Unprotected)			
109268	1	0	3.12	56.4	153
109276	1	1	2.91	49.9	131
109300	4	0	2.66	29.5	72
110705	4	4	2.97	50.7	131

Table 54 (Continued)

DATA ON ACLAR-PROTECTED SAMPLES STORED UNDER VARIOUS CONDITIONS

(Discharge at 10 mA/cm^2, Cathode is 17% carbon, 1 hr P-K blend)

Ambient, Total Cell Encapsulation

Cell	Storage Time (weeks)	Average Voltage (V)	Efficiency (%)	Energy Density (w-hr/lb)
110735	12	3.14	56.0	152
110736	12	3.09	57.0	155

Ambient, Lithium Encapsulation

Cell	Storage Time (weeks)		Average Voltage (V)	Cathode Efficiency (%)	Energy Density (w-hr/lb)
	Li (Aclar Protected)	Cathode (Unprotected)			
110738	12	0	3.13	54.7	149
110737	12	12	3.17	53.2	129

70°F, 50% Relative Humidity, Total Cell Encapsulation

Cell	Storage Time (weeks)	Average Voltage (V)	Efficiency (%)	Energy Density (w-hr/lb)
110745	12	3.11	59.3	153
110746	12	3.14	58.7	153

70°F, 50% Relative Humidity, Lithium Encapsulation

Cell	Storage Time (weeks)		Average Voltage (V)	Cathode Efficiency (%)	Energy Density (w-hr/lb)
	Li (Aclar Protected)	Cathode (Unprotected)			
110747	12	0	2.88	48.8	125*
110751	12	12	2.86	23.0	51

* Inadvertently left at open circuit for 1 hour before discharge.

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III. APPENDIX TABLES

Appendix Table A-1

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Sample Characteristics			Applied Pressure	Sample Height (cm)		Sample Density (g/cm³)		Sample Potential(c) (volts)		Sample Conductivity(d) (ohm⁻¹ cm⁻¹)	
Number	Composition	Blending(g)	(lb/in²)	P(a)	N(b)	P	N	P	N	P	N
105061a	0.28 g SAB	Waring (1.0 min)	100	0.17		0.32		0.0027		1.74	
			200	0.15	NM(e)	0.37	NM	0.0016	NM	1.85	NM
			500	0.12		0.46		0.0007		3.39	
			1,000	0.10		0.55		0.0004		4.82	
			2,000	0.07		0.79		0.0003		5.14	
105083	1.12 g SAB	Waring (1.0 min)	3	1.84		0.12	0.12	0.120		0.30	0.30
			10	1.32	1.38	0.17	0.16	0.044	0.052	0.59	0.53
			20	1.08	1.18	0.21	0.19	0.025	0.036	0.86	0.65
			100	0.72	0.92	0.31	0.24	0.0083	0.0216	1.72	0.84
			200	0.60	0.80	0.37	0.28	0.0048	0.0183	2.48	0.87
			500	0.44	0.70	0.50	0.32	0.0025	0.0165	3.48	0.84
			1,000	0.38	0.60	0.58	0.37	0.0015	0.0165	5.00	0.72
			2,000	0.30	0.52	0.74	0.43	0.00088	0.0087	6.75	1.18
			5,000	0.22	0.42	1.01	0.53	0.00047	0.0150	9.27	5.54
			10,000	0.18	0.38	1.23	0.58	0.00032	0.0114	11.12	6.60
105084	1.12 g SAB 0.08 g CF	Waring (1.0 min)	3	1.90		0.12		0.120		0.31	
			10	1.36	1.40	0.17	0.17	0.044	0.049	0.61	0.57
			20	1.10	1.20	0.22	0.20	0.0253	0.039	0.86	0.61
			100	0.76	0.94	0.31	0.25	0.0094	0.0214	1.60	0.87
			200	0.60	0.80	0.40	0.30	0.0048	0.0171	2.44	0.92
			500	0.49	0.70	0.48	0.34	0.00218	0.0142	4.45	0.98
			1,000	0.40	0.60	0.59	0.40	0.00125	0.0136	6.34	0.87
			2,000	0.30	0.49	0.79	0.48	0.00074	0.0088	8.04	1.10
			5,000	0.24	0.44	0.99	0.54	0.00040	0.0068	11.90	1.28
			10,000	0.20	0.40	1.18	0.59	0.00029	0.0076	13.60	1.04
105061b	1.50 g DCA-70 0.28 g SAB 0.04 g CF	Waring (0.5 min)	100	0.51		0.70		0.026		0.39	
			200	0.42		0.85		0.024		0.35	
			500	0.40	NM	0.89	NM	0.015	NM	0.53	NM
			1,000	0.34		1.05		0.010		0.67	
			2,000	0.32		1.11		0.007		0.92	
105063	3.00 g DCA-70 0.56 g SAB 0.04 g CF	Waring (0.5 min)	100	0.94		0.76		0.056		0.33	
			200	0.86		0.83		0.043		0.40	
			500	0.76	NM	0.94	NM	0.027	NM	0.56	NM
			1,000	0.68		1.05		0.019		0.71	
			2,000	0.62		1.15		0.013		0.94	
			5,000	0.52		1.37		0.007		1.37	
			10,000	0.42		1.70		0.005		1.73	
105074	3.00 g DCA-70 0.60 g SAB	Waring (0.5 min)	10	1.38		0.52		0.260	0.320	0.10	
			20	1.13		0.63		0.145	0.192	0.15	
			100	0.90		0.79		0.051	0.068	0.35	
			200	0.88	NM	0.81	NM	0.042	0.065	0.42	NM
			500	0.80		0.89		0.027	0.049	0.59	
			1,000	0.70		1.02		0.019	0.042	0.73	
			2,000	0.66		1.08		0.013	0.037	1.00	
			5,000	(0.58)		(1.23)		0.006	0.024	1.77	
			10,000	(0.48)		(1.48)		0.004	0.020	2.16	

Appendix Table A-1 (Continued)

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Number	Sample Characteristics: Composition	Sample Characteristics: Blending[g]	Applied Pressure (lb/in²)	Sample Height (cm): P[a]	Sample Height (cm): N[b]	Sample Density (g/cm³): P	Sample Density (g/cm³): N	Sample Potential[c] (volts): P	Sample Potential[c] (volts): N	Sample Conductivity[d] (ohm⁻¹ cm⁻¹): P	Sample Conductivity[d] (ohm⁻¹ cm⁻¹): N
105075	3.00 g DCA-70[f] 0.60 g SAB	Waring (0.5 min)	10	1.15		0.62		0.161	0.166	0.14	
			20	1.05		0.68		0.114	0.132	0.18	
			100	0.88		0.81		0.047	0.082	0.37	
			200	0.82	NM	0.87	NM	0.038	0.073	0.43	NM
			500	0.70		1.02		0.025	0.061	0.55	
			1,000	0.65		1.10		0.017	0.038	0.76	
			2,000	0.58		1.23		0.012	0.032	0.96	
105076	Two batches combined 1.50 g DCA-70[f] 0.30 g SAB (Total 3.6 g)	Waring (each blended 0.5 min)	10	1.28	1.28	0.56	0.56	0.190	0.195	0.13	0.13
			20	1.12	1.14	0.64	0.62	0.130	0.140	0.17	0.16
			100	0.90	0.94	0.80	0.76	0.054	0.077	0.33	0.24
			200	0.80	0.86	0.88	0.82	0.038	0.070	0.42	0.24
			500	0.70	0.76	1.02	0.94	0.025	0.046	0.55	0.33
			1,000	0.60	0.68	1.18	1.04	0.018	0.040	0.66	0.34
			2,000	0.54	0.62	1.32	1.14	0.012	0.031	0.89	0.40
105077	10.0 g DCA-70 [f] 2.0 g SAB	Ball Mill (10.0 min)	10	1.18	1.18	0.60	0.60	0.210	0.210	0.11	0.11
			20	1.02	1.06	0.70	0.67	0.140	0.150	0.14	0.14
			100	0.82	0.88	0.87	0.81	0.049	0.073	0.33	0.24
			200	0.80	0.84	0.89	0.85	0.045	0.068	0.35	0.24
			500	0.70	0.76	1.02	0.94	0.027	0.053	0.51	0.28
			1,000	0.66	0.72	1.08	0.99	0.019	0.043	0.69	0.33
			2,000	0.60	0.66	1.19	1.08	0.013	0.034	0.91	0.38
105081	1.50 g DCA-70[f] 0.28 g SAB 0.02 g CF	Waring (0.5 min)	3	0.70	0.70	0.51	0.51	0.135	0.135	0.10	0.10
			10	0.58	0.58	0.61	0.61	0.069	0.073	0.17	0.15
			20	0.50	0.52	0.71	0.68	0.049	0.056	0.20	0.18
			100	0.42	0.44	0.85	0.81	0.024	0.034	0.35	0.25
			200	0.39	0.42	0.91	0.85	0.018	0.033	0.43	0.25
			500	0.36	0.40	0.99	0.89	0.013	0.029	0.55	0.27
			1,000	0.34	0.36	1.05	0.99	0.010	0.024	0.67	0.30
			2,000	0.28	0.32	1.27	1.11	0.0061	0.019	0.91	0.33
			5,000	0.23	0.28	1.55	1.27	0.0035	0.012	1.30	0.46
			10,000	0.20	0.24	1.78	1.48	0.0025	0.013	1.60	0.37
105082	1.50 g DCA-70[f] 0.28 g SAB	Waring (0.5 min)	3	0.70	0.70	0.50	0.50	0.150	0.150	0.09	0.09
			10	0.58	0.58	0.61	0.61	0.081	0.086	0.14	0.14
			20	0.50	0.52	0.70	0.68	0.056	0.065	0.18	0.16
			100	0.42	0.45	0.84	0.78	0.027	0.039	0.31	0.23
			200	0.39	0.41	0.90	0.86	0.019	0.032	0.41	0.25
			500	0.35	0.36	1.00	0.98	0.014	0.022	0.49	0.32
			1,000	0.32	0.34	1.10	1.04	0.0088	0.022	0.72	0.31
			2,000	0.28	0.31	1.25	1.13	0.0062	0.015	0.89	0.41
			5,000	0.22	0.28	1.60	1.25	0.0035	0.010	1.24	0.55
			10,000	0.20	0.26	1.76	1.41	0.0025	0.015	1.58	0.34

a Value under indicated pressure.
b Value after release of indicated pressure.
c Resistance of the sample (ohms) = 10X potential (volts) since 0.100 amp current used.
d Conductivity = sample height ÷ (sample resistance) (sample area = 5.06 cm²).
e Not measured.
f DCA-70 sample from K and K Chemical Co.
g In all Waring blender studies the carbon components were Waring blended for 1.0 min prior to the listed mixing time with any active chlorine component present.

Appendix Table A-2

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Number	Composition g	Composition %C	Blending Method Time	Applied Pressure (lb/in²)	Sample Height (cm) P[a]	Sample Height (cm) N[b]	Sample Density (g/cm³) P	Sample Density (g/cm³) N	Sample Potential[c] (volts) P	Sample Potential[c] (volts) N	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) P	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) N
105076	3.6	17	Waring 0.5 min	10	1.28	1.28	0.56	0.56	0.190	0.195	0.13	0.13
				20	1.12	1.14	0.64	0.62	0.130	0.140	0.17	0.16
				100	0.90	0.94	0.80	0.76	0.054	0.077	0.33	0.24
				200	0.80	0.86	0.88	0.82	0.038	0.070	0.42	0.24
				500	0.70	0.76	1.02	0.94	0.025	0.046	0.55	0.33
				1,000	0.60	0.68	1.18	1.04	0.018	0.040	0.66	0.34
				2,000	0.54	0.62	1.32	1.14	0.012	0.031	0.89	0.40
105086	3.0	17	Waring 1.0 min	3	1.12	----	0.530	----	0.59	-----	0.037	----
				10	0.92	0.94	0.645	0.63	0.26	0.29	0.070	0.064
				20	0.84	0.88	0.706	0.67	0.17	0.23	0.098	0.076
				100	0.70	0.70	0.849	0.84	0.091	0.22	0.152	0.063
				200	0.62	0.64	0.958	0.91	0.052	0.10	0.236	0.127
				500	0.56	0.60	1.06	0.99	0.039	0.081	0.284	0.147
				1,000	0.51	0.58	1.16	1.02	0.020	0.051	0.497	0.225
				2,000	0.47	0.54	1.26	1.10	0.012	0.055	0.74	0.191
				5,000	0.40	0.46	1.48	1.29	0.006	0.027	1.20	0.337
				10,000	0.36	0.42	1.65	1.41	0.004	0.021	1.74	0.396
105087	3.0	17	Waring 2.0 min	3	1.10	----	0.539	----	0.54	-----	0.040	-----
				10	0.88	0.90	0.675	0.66	0.26	0.27	0.067	0.066
				20	0.82	0.82	0.724	0.72	0.18	0.20	0.090	0.081
				100	0.70	0.70	0.848	0.84	0.075	0.107	0.185	0.128
				200	0.62	0.64	0.958	0.92	0.050	0.081	0.246	0.157
				500	0.56	0.60	1.06	0.98	0.031	0.059	0.358	0.202
				1,000	0.50	0.56	1.19	1.06	0.020	0.049	0.496	0.226
				2,000	0.48	0.50	1.24	1.19	0.014	0.034	0.68	0.291
				5,000	0.40	0.44	1.48	1.35	0.006	0.026	1.18	0.435
				10,000	0.36	0.42	1.65	1.41	0.004	0.018	1.74	0.448
105088	3.0	17	Waring 5.0 min	3	1.04	----	0.570	----	0.81	-----	0.025	-----
				10	0.88	0.88	0.674	0.67	0.33	0.35	0.052	0.049
				20	0.80	0.80	0.942	0.74	0.21	0.24	0.075	0.064
				100	0.60	0.62	0.990	0.95	0.059	0.086	0.202	0.143
				200	0.59	0.60	1.01	0.99	0.055	0.084	0.212	0.141
				500	0.54	0.59	1.10	1.01	0.037	0.067	0.289	0.177
				1,000	0.51	0.54	1.16	1.10	0.024	0.058	0.422	0.184
				2,000	0.48	0.50	1.24	1.19	0.015	0.041	0.63	0.242
				5,000	0.39	0.42	1.52	1.41	0.007	0.024	1.10	0.340
				10,000	0.34	0.40	1.74	1.48	0.004	0.023	1.57	0.337

Appendix Table A-2 (continued)

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Number	Composition g	Composition %C	Blending Method Time	Applied Pressure (lb/in²)	Sample Height (cm) P(a)	Sample Height (cm) N(b)	Sample Density (g/cm³) P	Sample Density (g/cm³) N	Sample Potential(c) (volts) P	Sample Potential(c) (volts) N	Sample Conductivity(d) (ohm⁻¹ cm⁻¹) P	Sample Conductivity(d) (ohm⁻¹ cm⁻¹) N
105089	3.0	17	Waring	3	0.98	----	0.605	-----	1.07	----	0.018	-----
			10 min	10	0.81	0.81	0.733	0.733	0.52	0.54	0.030	0.029
				20	0.74	0.76	0.792	0.782	0.34	0.38	0.043	0.039
				100	0.62	0.64	0.958	0.928	0.13	0.175	0.095	0.072
				200	0.58	0.60	1.02	0.990	0.072	0.12	0.160	0.099
				500	0.52	0.56	1.14	1.06	0.046	0.088	0.224	0.126
				1,000	0.49	0.50	1.21	1.19	0.029	0.064	0.334	0.155
				2,000	0.44	0.49	1.35	1.21	0.018	0.045	0.484	0.216
				5,000	0.39	0.44	1.52	1.35	0.007	0.025	0.99	0.340
				10,000	0.34	0.40	1.75	1.48	0.004	0.018	1.50	0.428
105085	3.6	17	P-K	3	1.41	----	0.505	-----	12.7	------	0.002	-----
			20 min	10	1.21	1.21	0.588	0.588	5.50	5.50	0.004	0.004
			No fibers	20	1.06	1.10	0.672	0.647	3.30	3.40	0.006	0.006
				100	0.75	0.78	0.950	0.912	0.92	1.09	0.016	0.044
				200	0.71	0.76	1.00	0.937	0.85	0.95	0.016	0.015
				500	0.70	0.76	1.02	0.937	0.80	0.99	0.017	0.015
				1,000	0.68	0.70	1.05	1.02	0.61	0.93	0.022	0.014
				2,000	0.60	0.64	1.19	1.11	0.43	0.70	0.027	0.018
				5,000	0.50	0.59	1.43	1.21	0.24	0.46	0.041	0.025
				10,000	0.44	0.52	1.62	1.37	0.15	0.35	0.058	0.029
109201a	3.0	17	P-K	3	1.39	----	0.427	-----	0.571	-----	0.048	-----
			1 hour	10	1.15	1.15	0.506	0.506	0.292	0.294	0.078	0.077
				20	0.99	1.00	0.599	0.593	0.178	0.214	0.110	0.092
				50	0.83	0.86	0.715	0.690	0.103	0.132	0.160	0.129
				100	0.76	0.79	0.782	0.752	0.070	0.108	0.214	0.145
				200	0.67	0.72	0.885	0.824	0.048	0.085	0.275	0.168
				500	0.59	0.65	1.01	0.913	0.031	0.063	0.368	0.203
				1,000	0.53	0.59	1.12	1.01	0.021	0.052	0.496	0.223
				2,000	0.47	0.53	1.26	1.12	0.014	0.045	0.651	0.234
109201b	3.0	17	P-K	3	1.39	----	0.427	-----	0.550	------	0.045	-----
			1 hour	10	1.11	1.12	0.534	0.530	0.256	0.267	0.086	0.083
				20	0.97	0.98	0.612	0.606	0.163	0.184	0.118	0.105
				50	0.84	0.87	0.706	0.682	0.095	0.130	0.175	0.133
				100	0.75	0.80	0.791	0.742	0.066	0.108	0.222	0.147
				200	0.67	0.74	0.885	0.802	0.047	0.084	0.282	0.174
				500	0.59	0.66	1.01	0.899	0.030	0.064	0.387	0.203
				1,000	0.53	0.61	1.12	0.974	0.020	0.051	0.505	0.235
				2,000	0.47	0.54	1.26	1.10	0.013	0.040	0.700	0.267
109203	3.0	17	P-K	3	1.41	----	0.420	-----	0.56	------	0.049	-----
			1 hour	10	1.11	1.12	0.534	0.529	0.260	0.281	0.084	0.078
				20	0.99	1.00	0.599	0.593	0.169	0.198	0.115	0.100
				50	0.85	0.89	0.698	0.666	0.098	0.140	0.172	0.126
				100	0.76	0.81	0.780	0.732	0.069	0.120	0.218	0.134
				200	0.69	0.75	0.859	0.791	0.048	0.089	0.281	0.166
				500	0.60	0.68	0.988	0.872	0.031	0.064	0.383	0.209
				1,000	0.55	0.60	1.078	0.988	0.021	0.056	0.519	0.226
				2,000	0.48	0.56	1.235	1.059	0.014	0.042	0.669	0.264

Appendix Table A-2 (continued)

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Number	Composition g	Composition %C	Blending Method Time	Applied Pressure (lb/in²)	Sample Height (cm) P[a]	Sample Height (cm) N[b]	Sample Density (g/cm³) P	Sample Density (g/cm³) N	Sample Potential[c] (volts) P	Sample Potential[c] (volts) N	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) P	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) N
105095	3.0	17	P-K 8 hours	3	1.32	-----	0.450	-----	0.72	-----	0.036	-----
				10	1.06	1.08	0.561	0.550	0.30	0.31	0.069	0.069
				20	0.92	0.95	0.656	0.626	0.180	0.208	0.101	0.090
				100	0.71	0.79	0.838	0.752	0.078	0.118	0.180	0.133
				200	0.66	0.71	0.900	0.838	0.053	0.092	0.244	0.153
				500	0.57	0.64	1.04	0.929	0.033	0.066	0.342	0.192
				1,000	0.50	0.60	1.19	0.990	0.021	0.050	0.460	0.238
				2,000	0.45	0.53	1.32	1.12	0.014	0.043	0.610	0.244
				5,000	0.36	0.45	1.65	1.32	0.007	0.032	0.938	0.274
				10,000	0.31	0.40	1.92	1.49	0.004	0.030	1.334	0.264
105094	3.0	17	P-K 24 hours	3	1.31	----	0.453	-----	1.27	-----	0.020	-----
				10	1.08	1.09	0.550	0.545	0.52	0.52	0.041	0.041
				20	0.93	0.98	0.639	0.606	0.37	0.38	0.049	0.051
				100	0.74	0.80	0.804	0.742	0.086	0.14	0.170	0.113
				200	0.68	0.73	0.874	0.814	0.058	0.107	0.232	0.135
				500	0.60	0.69	0.990	0.861	0.038	0.083	0.313	0.165
				1,000	0.53	0.61	1.12	0.975	0.025	0.074	0.413	0.163
				2,000	0.49	0.55	1.21	1.08	0.016	0.072	0.588	0.151
				5,000	0.39	0.49	1.52	0.21	0.008	0.041	0.878	0.237
				10,000	0.34	0.42	1.75	1.41	0.005	0.029	1.224	0.287
105090	3.0	17	B-M 10 min	3	1.11	----	0.535	------	0.51	-----	0.043	-----
				10	0.96	0.96	0.619	0.619	0.27	0.29	0.070	0.066
				20	0.88	0.89	0.675	0.668	0.18	0.20	0.097	0.088
				100	0.70	0.72	0.850	0.825	0.072	0.108	0.193	0.132
				200	0.64	0.70	0.929	0.850	0.048	0.084	0.264	0.165
				500	0.59	0.61	1.01	0.974	0.030	0.063	0.390	0.192
				1,000	0.51	0.58	1.16	1.02	0.020	0.054	0.50	0.212
				2,000	0.48	0.51	1.24	1.16	0.012	0.041	0.75	0.246
				5,000	0.40	0.45	1.49	1.32	0.006	0.034	1.16	0.262
				10,000	0.35	0.40	1.70	1.49	0.004	0.037	1.65	0.214
105091	3.0	17	B-M 1 hour	3	0.91	----	0.653	-----	1.29	-----	0.014	-----
				10	0.80	0.81	0.743	0.733	0.65	0.68	0.024	0.024
				20	0.75	0.75	0.792	0.792	0.45	0.49	0.033	0.030
				100	0.64	0.66	0.929	0.900	0.165	0.250	0.076	0.052
				200	0.59	0.61	1.01	0.974	0.104	0.184	0.112	0.066
				500	0.54	0.56	1.10	1.06	0.061	0.137	0.174	0.081
				1,000	0.50	0.52	1.19	1.14	0.037	0.093	0.268	0.111
				2,000	0.46	0.50	1.29	1.19	0.021	0.078	0.424	0.127
				5,000	0.40	0.42	1.48	1.41	0.008	0.057	0.932	0.146
				10,000	0.36	0.40	1.65	1.48	0.005	0.069	1.370	0.115
82865	Repeat of above - week later			3	0.92	----	0.638	-----	1.98	-----	0.009	-----
				10	0.81	0.81	0.732	0.732	0.93	1.00	0.017	0.016
				20	0.74	0.76	0.802	0.780	0.607	0.712	0.024	0.021
				50	0.67	0.69	0.885	0.860	0.355	0.492	0.037	0.027
				100	0.63	0.65	0.942	0.912	0.247	0.390	0.050	0.033
				200	0.59	0.62	1.01	0.956	0.152	0.285	0.076	0.043
				500	0.53	0.56	1.12	1.06	0.084	0.193	0.125	0.057
				1,000	0.49	0.53	1.21	1.12	0.049	0.137	0.196	0.076
				2,000	0.44	0.48	1.35	1.24	0.028	0.096	0.309	0.119

Appendix Table A-2 (continued)

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Number	Composition g	%C	Blending Method Time	Applied Pressure (lb/in^2)	Sample Height (cm) P[a]	N[b]	Sample Density (g/cm^3) P	N	Sample Potential[c] (volts) P	N	Sample Conductivity[d] (ohm^{-1} cm^{-1}) P	N
105097a	Repeat of above New sample			3	0.98	----	0.606	-----	3.65	-----	0.005	-----
				10	0.79	0.81	0.752	0.733	1.64	1.74	0.009	0.009
				20	0.74	0.76	0.803	0.782	1.04	1.18	0.014	0.012
				100	0.65	0.67	0.914	0.887	0.35	0.53	0.036	0.025
				200	0.60	0.63	0.990	0.944	0.21	0.372	0.056	0.033
				500	0.53	0.57	1.12	1.04	0.098	0.220	0.107	0.051
				1,000	0.48	0.53	1.24	1.12	0.054	0.145	0.176	0.072
				2,000	0.43	0.48	1.38	1.24	0.028	0.093	0.299	0.102
				5,000	0.35	0.44	1.70	1.35	0.011	0.045	0.630	0.194
				10,000	0.30	0.39	1.98	1.52	0.006	0.032	0.966	0.238
105097b	Repeat of above Same sample			3	0.96	----	0.619	-----	2.49	------	0.007	-----
				10	0.83	0.84	0.716	0.708	1.16	1.20	0.014	0.013
				20	0.78	0.79	0.762	0.752	0.73	0.83	0.021	0.018
				100	0.67	0.71	0.885	0.835	0.25	0.39	0.053	0.036
				200	0.59	0.63	1.01	0.944	0.165	0.285	0.071	0.043
				500	0.54	0.57	1.10	1.04	0.088	0.172	0.122	0.065
				1,000	0.47	0.53	1.26	1.12	0.049	0.113	0.189	0.095
				2,000	0.43	0.48	1.38	1.24	0.028	0.081	0.304	0.117
				5,000	0.35	0.43	1.70	1.38	0.011	0.046	0.630	0.185
				10,000	0.32	0.38	1.86	1.54	0.006	0.030	0.975	0.251
82857	Repeat of above Same sample			3	0.94	----	0.631	-----	3.84	-----	0.004	-----
				10	0.82	0.84	0.724	0.706	1.76	1.93	0.009	0.008
				20	0.76	0.77	0.782	0.770	1.14	1.44	0.013	0.010
				50	0.70	0.73	0.848	0.812	0.675	0.990	0.020	0.014
				100	0.65	0.68	0.912	0.872	0.401	0.715	0.032	0.018
				200	0.60	0.64	0.989	0.927	0.242	0.494	0.049	0.025
				500	0.54	0.57	1.10	1.04	0.114	0.296	0.093	0.038
				1,000	0.47	0.53	1.26	1.07	0.062	0.137	0.150	0.056
				2,000	0.42	0.47	1.41	1.26	0.033	0.137	0.252	0.067
				5,000								
82865	Repeat of above New sample			3	0.88	----	0.673	-----	3.10	-----	0.005	-----
				10	0.77	0.79	0.770	0.751	1.60	1.73	0.009	0.009
				20	0.72	0.74	0.824	0.801	1.03	1.28	0.013	0.011
				50	0.66	0.68	0.898	0.872	0.621	0.960	0.021	0.014
				100	0.62	0.64	0.956	0.927	0.409	0.727	0.030	0.017
				200	0.59	0.61	1.01	0.972	0.251	0.538	0.046	0.022
				500	0.53	0.56	1.12	1.06	0.122	0.339	0.086	0.032
				1,000	0.50	0.52	1.19	1.14	0.068	0.222	0.145	0.046
				2,000	0.44	0.47	1.35	1.26	0.036	0.143	0.241	0.065
105096	3.0	17	B-M 8 hours	3	0.90	----	0.660	-----	12.1	-----	0.000	------
				10	0.80	0.81	0.743	0.733	4.15	4.55	0.000	0.000
				20	0.72	0.73	0.826	0.814	17.0	21.3	0.000	0.000
				100	0.65	0.68	0.915	0.874	5.80	9.10	0.002	0.001
				200	0.60	0.65	0.990	0.915	3.41	6.10	0.003	0.002
				500	0.56	0.60	1.06	0.990	1.48	3.30	0.007	0.003
				1,000	0.50	0.55	1.19	1.08	0.84	2.12	0.011	0.005
				2,000	0.47	0.51	1.27	1.17	0.385	1.10	0.024	0.009
				5,000	0.40	0.46	1.49	1.29	0.116	0.47	0.068	0.019
				10,000	0.36	0.40	1.65	1.49	0.050	0.229	0.143	0.034

Appendix Table A-2 (continued)

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Number	Composition g	Composition %C	Blending Method Time	Applied Pressure (lb/in²)	Sample Height (cm) P[a]	Sample Height (cm) N[b]	Sample Density (g/cm³) P	Sample Density (g/cm³) N	Sample Potential[c] (volts) P	Sample Potential[c] (volts) N	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) P	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) N
105093	3.0	17	B-M	3	0.82	----[e]	0.725	-----	NM	-----	NM	-----
			24 hours	10	0.70	NM	0.849	NM	NM	NM	NM	NM
				20	0.61	NM	0.975	NM	NM	NM	NM	NM
				100	0.58	NM	1.02	NM	NM	NM	NM	NM
				200	0.56	NM	1.06	NM	21.5	NM	0.000	NM
				500	0.52	0.54	1.14	1.10	11.2	20.8	0.000	0.000
				1,000	0.48	0.50	1.24	1.19	5.71	12.0	0.001	0.000
				2,000	0.41	0.45	1.45	1.32	2.50	5.60	0.003	0.001
				5,000	0.34	0.40	1.75	1.49	0.41	1.59	0.016	0.004
				10,000	0.30	0.37	1.98	1.60	0.164	1.11	0.036	0.006
82856	3.0	24	Waring	3	1.51	----	0.393	-----	0.209	-----	0.143	------
			0.5 min	10	1.18	1.20	0.502	0.494	0.094	0.118	0.248	0.201
				20	1.05	1.07	0.565	0.554	0.068	0.093	0.306	0.228
				50	0.90	0.96	0.659	0.617	0.037	0.066	0.312	0.288
				100	0.82	0.88	0.722	0.673	0.027	0.070	0.601	0.249
				200	0.73	0 80	0.812	0.741	0.019	0.071	0.761	0.223
				500	0.63	0.86	0.946	0.688	0.013	0.086	0.959	0.198
				1,000	0.56	0.64	1.06	0.927	0.009	0.077	1.205	0.164
				2,000	0.50	0.57	1.19	1.04	0.005	0.055	1.737	0.205
82859	3.0	24	Waring	3	1.25	----	0.475	-----	0.254	-----	0.101	-----
			2.0 min	10	1.13	1.14	0.525	0.521	0.172	0.183	0.130	0.123
				20	0.99	1.02	0.600	0.582	0.109	0.135	0.179	0.149
				50	0.89	0.93	0.666	0.638	0.071	0.092	0.248	0.188
				100	0.80	0.84	0.742	0.706	0.046	0.074	0.344	0.225
				200	0.72	0.77	0.824	0.771	0.031	0.061	0.459	0.249
				500	0.62	0.67	0.958	0.886	0.017	0.045	0.698	0.295
				1,000	0.56	0.62	1.06	0.958	0.011	0.032	0.939	0.384
				2,000	0.51	0.57	1.16	1.04	0.007	0.025	1.329	0.451
82863	3.0	24	P-K	3	1.73	----	0.343	-----	0.310	-----	0.111	-----
			1 hour	10	1.34	1.36	0.443	0.437	0.133	0.137	0.199	0.197
				20	1.15	1.19	0.517	0.498	0.085	0.098	0.268	0.241
				50	0.98	1.05	0.605	0.565	0.052	0.072	0.372	0.289
				100	0.87	0.94	0.682	0.632	0.035	0.057	0.481	0.324
				200	0.75	0.85	0.791	0.698	0.024	0.045	0.616	0.369
				500	0.64	0.75	0.928	0.791	0.015	0.035	0.839	0.415
				1,000	0.58	0.66	1.02	0.900	0.010	0.027	1.104	0.468
				2,000	0.51	0.59	1.16	1.01	0.007	0.022	1.383	0.515
82861	3.0	24	P-K	3	1.63	----	0.364	-----	0.490	------	0.066	-----
			8 hours	10	1.28	1.29	0.463	0.460	0.208	0.217	0.122	0.118
				20	1.13	1.16	0.525	0.512	0.135	0.158	0.166	0.145
				50	0.97	1.02	0.612	0.582	0.078	0.113	0.244	0.179
				100	0.85	0.92	0.698	0.645	0.050	0.082	0.333	0.221
				200	0.75	0.83	0.791	0.715	0.032	0.062	0.458	0.265
				500	0.64	0.73	0.928	0.812	0.018	0.044	0.670	0.323
				1,000	0.57	0.65	1.04	0.912	0.012	0.036	0.889	0.349
				2,000	0.51	0.59	1.16	1.01	0.008	0.029	1.172	0.403

Appendix Table A-2 (continued)

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Number	Composition g	Composition %C	Blending Method Time	Applied Pressure (lb/in²)	Sample Height (cm) P[a]	Sample Height (cm) N[b]	Sample Density (g/cm³) P	Sample Density (g/cm³) N	Sample Potential[c] (volts) P	Sample Potential[c] (volts) N	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) P	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) N
82866	3.0	24	B-M 1 hour	3	0.93	----	0.637	----	0.795	-----	0.023	-----
				10	0.79	0.80	0.750	0.741	0.369	0.382	0.042	0.041
				20	0.72	0.73	0.823	0.812	0.228	0.259	0.062	0.055
				50	0.64	0.66	0.927	0.898	0.136	0.170	0.093	0.076
				100	0.59	0.62	1.01	0.956	0.094	0.129	0.124	0.095
				200	0.55	0.57	1.08	1.04	0.057	0.102	0.188	0.111
				500	0.48	0.51	1.24	1.16	0.033	0.076	0.285	0.133
				1,000	0.43	0.46	1.38	1.29	0.021	0.069	0.392	0.131
				2,000	0.39	0.42	1.52	1.41	0.013	0.091	0.564	0.091
82868	3.0	24	B-M 8 hours	3	0.70	----	0.751	-----	3.43	-----	0.004	-----
				10	0.72	0.72	0.823	0.823	1.96	2.02	0.007	0.007
				20	0.65	0.67	0.912	0.885	1.27	1.37	0.010	0.009
				50	0.59	0.61	1.01	0.973	0.720	0.819	0.016	0.014
				100	0.55	0.56	1.08	1.06	0.489	0.601	0.022	0.018
				200	0.49	0.50	1.21	1.19	0.279	0.400	0.034	0.024
				500	0.43	0.44	1.38	1.35	0.133	0.333	0.064	0.026
				1,000	0.38	0.40	1.56	1.48	0.067	0.267	0.112	0.029
				2,000	0.34	0.36	1.74	1.65	0.032	0.213	0.209	0.033
82854	3.0	10	Waring 0.5 min	3	0.90	----	0.658	-----	0.75	-----	0.023	-----
				10	0.77	0.78	0.769	0.760	0.425	0.433	0.035	0.035
				20	0.71	0.73	0.836	0.810	0.320	0.339	0.043	0.042
				50	0.65	0.67	0.912	0.885	0.240	0.255	0.053	0.052
				100	0.61	0.63	0.973	0.941	0.165	0.205	0.073	0.060
				200	0.57	0.58	1.04	1.02	0.114	0.162	0.099	0.070
				500	0.54	0.55	1.10	1.08	0.081	0.124	0.132	0.084
				1,000	0.49	0.51	1.21	1.16	0.056	0.107	0.173	0.094
				2,000	0.45	0.47	1.32	1.26	0.038	0.075	0.234	0.124
82855	3.0	10	Waring 2.0 min	3	0.87	----	0.682	-----	1.420	-----	0.012	-----
				10	0.76	0.77	0.780	0.770	0.820	0.840	0.018	0.018
				20	0.70	0.71	0.847	0.835	0.581	0.620	0.023	0.022
				50	0.64	0.66	0.927	0.898	0.382	0.463	0.033	0.028
				100	0.62	0.63	0.957	0.942	0.296	0.400	0.041	0.031
				200	0.57	0.59	1.04	1.01	0.211	0.320	0.053	0.036
				500	0.53	0.55	1.12	1.08	0.128	0.221	0.081	0.049
				1,000	0.48	0.51	1.24	1.16	0.082	0.157	0.116	0.064
				2,000	0.45	0.47	1.32	1.26	0.047	0.112	0.189	0.083
82862	3.0	10	P-K 1 hour	3	1.05	----	0.575	-----	0.755	-----	0.027	-----
				10	0.87	0.88	0.683	0.674	0.397	0.400	0.043	0.043
				20	0.78	0.80	0.761	0.742	0.272	0.298	0.056	0.053
				50	0.71	0.72	0.836	0.815	0.177	0.211	0.079	0.067
				100	0.65	0.67	0.914	0.887	0.136	0.174	0.094	0.076
				200	0.60	0.63	0.989	0.942	0.102	0.143	0.116	0.087
				500	0.54	0.58	1.10	1.02	0.070	0.112	0.153	0.102
				1,000	0.50	0.55	1.19	1.08	0.052	0.093	0.189	0.117
				2,000	0.45	0.48	1.32	1.24	0.033	0.071	0.264	0.133

Appendix Table A-2 (continued)

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Number	Composition g	Composition %C	Blending Method Time	Applied Pressure (lb/in²)	Sample Height (cm) P[a]	Sample Height (cm) N[b]	Sample Density (g/cm³) P	Sample Density (g/cm³) N	Sample Potential[c] (volts) P	Sample Potential[c] (volts) N	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) P	Sample Conductivity[d] (ohm⁻¹ cm⁻¹) N
82854	3.0	10	Waring 0.5 min	3	0.90	----	0.658	-----	0.75	-----	0.023	-----
				10	0.77	0.78	0.769	0.760	0.425	0.433	0.035	0.035
				20	0.71	0.73	0.836	0.810	0.320	0.339	0.043	0.042
				50	0.65	0.67	0.912	0.885	0.240	0.255	0.053	0.052
				100	0.61	0.63	0.973	0.941	0.165	0.205	0.073	0.060
				200	0.57	0.58	1.04	1.02	0.114	0.162	0.099	0.070
				500	0.54	0.55	1.10	1.08	0.081	0.129	0.132	0.084
				1,000	0.49	0.51	1.21	1.16	0.056	0.107	0.173	0.094
				2,000	0.45	0.47	1.32	1.26	0.038	0.075	0.234	0.124
82855	3.0	10	Waring 2.0 min	3	0.87	----	0.682	-----	1.420	-----	0.012	-----
				10	0.76	0.77	0.780	0.770	0.820	0.840	0.018	0.018
				20	0.70	0.71	0.847	0.835	0.581	0.620	0.023	0.022
				50	0.64	0.66	0.927	0.898	0.382	0.463	0.033	0.028
				100	0.62	0.63	0.957	0.942	0.296	0.400	0.041	0.031
				200	0.57	0.59	1.04	1.01	0.211	0.320	0.053	0.036
				500	0.53	0.55	1.12	1.08	0.128	0.221	0.081	0.049
				1,000	0.48	0.51	1.24	1.16	0.082	0.157	0.116	0.064
				2,000	0.45	0.47	1.32	1.26	0.047	0.112	0.189	0.083
82862	3.0	10	P-K 1 hour	3	1.05	----	0.575	-----	0.755	-----	0.027	-----
				10	0.87	0.88	0.683	0.674	0.397	0.400	0.043	0.043
				20	0.78	0.80	0.761	0.742	0.272	0.298	0.056	0.053
				50	0.71	0.72	0.836	0.815	0.177	0.211	0.079	0.067
				100	0.65	0.67	0.914	0.887	0.136	0.174	0.094	0.076
				200	0.60	0.63	0.989	0.942	0.102	0.143	0.116	0.087
				500	0.54	0.58	1.10	1.02	0.070	0.112	0.153	0.102
				1,000	0.50	0.55	1.19	1.08	0.052	0.093	0.189	0.117
				2,000	0.45	0.48	1.32	1.24	0.033	0.071	0.264	0.133
82860	3.0	10	P-K 8 hours	3	1.07	----	0.555	-----	1.66	-----		-----
				10	0.88	0.89	0.675	0.667	0.738	0.744	0.012	0.023
				20	0.79	0.81	0.752	0.732	0.484	0.520	0.023	0.030
				50	0.72	0.73	0.824	0.813	0.319	0.378	0.032	0.038
				100	0.65	0.67	0.912	0.885	0.231	0.303	0.044	0.043
				200	0.61	0.64	0.972	0.927	0.172	0.251	0.070	0.050
				500	0.55	0.58	1.08	1.02	0.111	0.184	0.098	0.062
				1,000	0.50	0.54	1.19	1.10	0.080	0.148	0.124	0.072
				2,000	0.45	0.49	1.32	1.21	0.051	0.118	0.174	0.082
82867	3.0	10	B-M 1 hour	3	0.88	----	0.673	-----	3.71[h]	-----	0.000	-----
				10	0.77	0.77	0.770	0.770	1.65[h]	1.67	0.000	0.000
				20	0.71	0.72	0.835	0.824	0.890[h]	0.92	0.001	0.001
				50	0.64	0.55	0.926	0.912	0.442[h]	0.475	0.002	0.002
				100	0.60	0.61	0.989	0.971	2.575	3.160	0.004	0.003
				200	0.55	0.56	1.08	1.06	1.720	2.12	0.006	0.005
				500	0.48	0.50	1.24	1.19	0.821	1.13	0.011	0.008
				1,000	0.44	0.47	1.35	1.26	0.482	0.733	0.018	0.012
				2,000	0.41	0.44	1.45	1.35	0.232	0.440	0.034	0.019

Appendix Table A-2 (continued)

EFFECT OF BLENDING TECHNIQUE ON CATHODE MIX CONDUCTIVITY AND DENSITY

Number	Composition g	Composition %C	Blending Method Time	Applied Pressure (lb/in^2)	Sample Height (cm) P[a]	Sample Height (cm) N[b]	Sample Density (g/cm^3) P	Sample Density (g/cm^3) N	Sample Potential[c] (volts) P	Sample Potential[c] (volts) N	Sample Conductivity[d] (ohm^{-1} cm^{-1}) P	Sample Conductivity[d] (ohm^{-1} cm^{-1}) N
82864	3.0	10	B-M	3	0.80	----	0.742	-----	7.72[h]	-----	0.000	-----
			8 hours	10	0.73	0.73	0.812	0.812	4.84[h]	5.05	0.000	0.000
				20	0.67	0.67	0.885	0.885	3.58[h]	3.79	0.000	0.000
				50	0.61	0.61	0.971	0.971	1.83[h]	2.02	0.000	0.000
				100	0.56	0.57	1.06	1.04	1.27[h]	1.47	0.000	0.000
				200	0.50	0.51	1.19	1.16	0.670[h]	0.860	0.001	0.001
				500	0.44	0.45	1.35	1.32	0.303[h]	0.450	0.002	0.001
				1,000	0.40	0.42	1.48	1.41	1.38	2.37	0.005	0.003
				2,000	0.37	0.39	1.60	1.52	1.820	1.75	0.008	0.004

a Value under indicated pressure

b Value after release of indicated pressure - 3 psi remains

c Resistance of the sample (ohms) - 10X potential (volts) since 0.100 amp current used.

d Conductivity - sample height ÷ (sample resistance)(sample area - 5.06 cm^2).

e Not measured

h Voltage at 10mA

Appendix Table A-3

EFFECT OF BLENDING TECHNIQUE ON MIX CONDUCTIVITY AND DENSITY

Sample Characteristics			Applied Pressure	Sample Height (cm)		Sample Density (g/cm³)		Sample Potential[c] (volts)		Sample Conductivity (ohm⁻¹ cm⁻¹)	
Number	Composition	Blending	(lb/in²)	P[a]	N[b]	P	N	P	N	P	N
109205	17% Carbon	PK 8 hrs	3	1.42	----	0.418	-----	1.14	----	0.024	----
			10	1.11	1.12	0.534	0.529	0.412	0.420	0.053	0.052
			20	0.97	0.98	0.611	0.605	0.237	0.272	0.081	0.071
			50	0.84	0.87	0.706	0.682	0.136	0.184	0.122	0.093
			100	0.75	0.80	0.791	0.741	0.090	0.142	0.164	0.112
			200	0.67	0.73	0.885	0.812	0.061	0.112	0.217	0.129
			500	0.60	0.65	0.988	0.912	0.037	0.083	0.320	0.155
			1000	0.54	0.60	1.099	0.988	0.024	0.061	0.431	0.192
			2000	0.48	0.54	1.235	1.099	0.015	0.046	0.605	0.231
109206	17% Carbon	BM 10 min	3	1.15	----	0.516	-----	1.32	-----	0.017	-----
			10	0.97	0.97	0.611	0.611	0.568	0.691	0.033	0.027
			20	0.87	0.89	0.682	0.666	0.341	0.419	0.050	0.042
			50	0.77	0.80	0.770	0.741	0.195	0.315	0.078	0.050
			100	0.71	0.74	0.835	0.801	0.132	0.244	0.107	0.060
			200	0.65	0.69	0.912	0.859	0.087	0.179	0.148	0.076
			500	0.59	0.63	1.005	0.941	0.046	0.131	0.249	0.095
			1000	0.53	0.57	1.119	1.040	0.285	0.081	0.368	0.139
			2000	0.48	0.53	1.235	1.119	0.017	0.064	0.537	0.162
109207	17% Carbon	PK 10 min	3	1.35	----	0.439	-----	0.221	-----	0.121	-----
			10	1.07	1.08	0.554	0.549	0.109	0.112	0.194	0.191
			20	0.94	0.98	0.605	0.605	0.073	0.084	0.254	0.229
			50	0.83	0.87	0.714	0.681	0.048	0.062	0.340	0.277
			100	0.77	0.81	0.770	0.732	0.037	0.052	0.410	0.307
			200	0.69	0.75	0.859	0.791	0.027	0.044	0.489	0.331
			500	0.62	0.68	0.956	0.872	0.018	0.037	0.653	0.361
			1000	0.54	0.61	1.098	0.972	0.013	0.036	0.775	0.331
			2000	0.50	0.57	1.186	1.04	0.009	0.025	1.010	0.441
109208	17% Carbon + 1% TFE	WB 0.5 min	3	1.24	----	0.478	-----	0.272	-----	0.090	-----
			10	0.99	1.01	0.599	0.587	0.141	0.147	0.139	0.136
			20	0.90	0.93	0.659	0.638	0.103	0.114	0.173	0.162
			50	0.81	0.85	0.732	0.698	0.068	0.086	0.234	0.195
			100	0.74	0.78	0.861	0.760	0.049	0.069	0.295	0.221
			200	0.67	0.72	0.885	0.824	0.036	0.057	0.364	0.249
			500	0.61	0.64	0.972	0.926	0.023	0.043	0.507	0.292
			1000	0.55	0.60	1.078	0.988	0.017	0.034	0.629	0.344
			2000	0.50	0.55	1.186	1.078	0.011	0.026	0.846	0.416
109209	17% Carbon + 3% TFE	WB 0.5 min	3	1.28	----	0.463	-----	0.268	-----	0.094	-----
			10	1.05	1.06	0.565	0.559	0.138	0.142	0.151	0.148
			20	0.93	0.95	0.638	0.624	0.096	0.108	0.192	0.174
			50	0.84	0.87	0.706	0.682	0.064	0.079	0.259	0.217
			100	0.78	0.80	0.760	0.741	0.048	0.065	0.320	0.241
			200	0.70	0.74	0.847	0.801	0.035	0.052	0.392	0.279
			500	0.62	0.66	0.956	0.898	0.022	0.038	0.541	0.342
			1000	0.57	0.61	1.040	0.972	0.015	0.030	0.719	0.892
			2000	0.51	0.55	1.163	1.078	0.010	0.025	0.990	0.424

Appendix Table A-3 (continued)

EFFECT OF BLENDING TECHNIQUE ON MIX CONDUCTIVITY AND DENSITY

Sample Characteristics			Applied Pressure	Sample Height (cm)		Sample Density (g/cm³)		Sample Potential[c] (volts)		Sample Conductivity (ohm⁻¹ cm⁻¹)	
Number	Composition	Blending	(lb/in²)	P[a]	N[b]	P	N	P	N	P	N
109218	17% Carbon + 5% TFE	WB 0.5 min	3	1.16	----	0.511	-----	9.437	-----	9.952	-----
			10	0.97	0.98	0.611	0.605	0.193	0.252	0.099	0.077
			20	0.88	0.89	0.674	0.666	0.130	0.225	0.134	0.078
			50	0.78	0.80	0.760	0.741	0.084	0.125	0.183	0.127
			100	0.71	0.75	0.835	0.791	0.062	0.114	0.226	0.130
			200	0.65	0.69	0.912	0.859	0.045	0.172	0.283	0.079
			500	0.57	0.62	1.04	0.956	0.029	0.193	0.387	0.063
			1000	0.52	0.57	1.14	1.04	0.020	0.248	0.507	0.045
			2000	0.46	0.51	1.29	1.16	0.013	0.173	0.660	0.058
109219	17% Carbon + 10% TFE	WB 0.5 min	3	1.15	----	0.516	-----	0.800	-----	0.028	-----
			10	0.94	0.95	0.630	0.624	0.450	0.755	0.008	0.005
			20	0.84	0.87	0.706	0.682	0.146[h]	0.855[h]	0.011	0.002
			50	0.76	0.78	0.780	0.760	0.061[h]	0.300[h]	0.024	0.005
			100	0.68	0.73	0.859	0.812	0.011[h]	0.086[h]	0.116	0.016
			200	0.63	0.68	0.941	0.872	0.006[h]	0.030[h]	0.210	0.044
			500	0.54	0.61	1.09	0.972	0.003[h]	0.018[h]	0.334	0.065
			1000	0.49	0.55	1.21	1.08	0.002[h]	0.018[h]	0.462	0.058
			2000	0.44	0.50	1.35	1.19	0.001[h]	0.029[h]	0.631	0.033
109210	17% Carbon + 1% Kynar	WB 0.5 min	3	1.38	----	0.429	-----	0.317	-----	0.086	-----
			10	1.07	1.08	0.554	0.549	0.142	0.143	0.149	0.149
			20	0.95	0.96	0.624	0.618	0.095	0.107	0.198	0.178
			50	0.82	0.86	0.723	0.689	0.060	0.073	0.270	0.232
			100	0.76	0.79	0.780	0.751	0.045	0.060	0.328	0.257
			200	0.69	0.73	0.859	0.812	0.033	0.043	0.414	0.330
			500	0.63	0.66	0.941	0.898	0.021	0.038	0.575	0.336
			1000	0.56	0.60	1.059	0.988	0.015	0.031	0.706	0.379
			2000	0.51	0.55	1.162	1.078	0.010	0.025	0.935	0.432
109210	17% Carbon + 3% Kynar	WB 0.5 min	3	1.33	----	0.446	-----	0.369	-----	0.071	-----
			10	1.05	1.06	0.565	0.559	0.162	0.168	0.128	0.125
			20	0.93	0.95	0.637	0.624	0.108	0.136	0.171	0.138
			50	0.83	0.86	0.714	0.689	0.068	0.089	0.239	0.191
			100	0.77	0.80	0.770	0.741	0.050	0.074	0.299	0.212
			200	0.70	0.73	0.847	0.812	0.036	0.057	0.376	0.249
			500	0.58	0.62	1.022	0.956	0.019	0.037	0.583	0.331
			1000	0.55	0.60	1.078	0.988	0.016	0.031	0.672	0.377
			2000	0.50	0.54	1.186	1.098	0.011	0.026	0.876	0.407
109229	17% Carbon + 10% Kynar	WB 0.5 min	3	1.22	----	0.486	-----	0.370	-----	0.065	-----
			10	1.05	1.06	0.565	0.559	0.211	0.229	0.099	0.092
			20	0.92	0.94	0.645	0.631	0.136	0.168	0.134	0.111
			50	0.80	0.84	0.741	0.706	0.079	0.128	0.199	0.129
			100	0.73	0.77	0.812	0.770	0.056	0.104	0.257	0.147
			200	0.67	0.72	0.885	0.824	0.041	0.081	0.323	0.175
			500	0.58	0.64	1.02	0.927	0.025	0.062	0.445	0.204
			1000	0.52	0.58	1.14	1.02	0.018	0.050	0.569	0.228
			2000	0.47	0.53	1.26	1.12	0.012	0.040	0.744	0.254

Appendix Table A-3 (continued)

EFFECT OF BLENDING TECHNIQUE ON MIX CONDUCTIVITY AND DENSITY

Sample Characteristics			Applied Pressure	Sample Height (cm)		Sample Density (g/cm^3)		Sample Potential[c] (volts)		Sample Conductivity (ohm^{-1} cm^{-1})	
Number	Composition	Blending	(lb/in^2)	P[a]	N[b]	P	N	P	N	P	N
109220	17% Carbon + 1% PVC	WB 0.5 min	3	1.15	----	0.516	-----	0.455	-----	0.050	-----
			10	1.03	1.03	0.576	0.576	0.190	0.230	0.107	0.088
			20	0.92	0.93	0.645	0.638	0.125	0.137	0.146	0.134
			50	0.81	0.83	0.732	0.714	0.086	0.113	0.186	0.145
			100	0.73	0.77	0.812	0.770	0.063	0.095	0.229	0.159
			200	0.66	0.71	0.898	0.835	0.045	0.083	0.285	0.168
			500	0.59	0.64	1.01	0.927	0.028	0.097	0.413	0.131
			1000	0.54	0.58	1.09	1.02	0.019	0.103	0.548	0.111
			2000	0.48	0.53	1.24	1.12	0.013	0.060	0.725	0.174
109220	17% Carbon + 3% PVC	WB 0.5 min	3	1.30	----	0.456	-----	1.04	-----	0.024	-----
			10	1.05	1.06	0.565	0.559	0.432	0.529	0.048	0.039
			20	0.93	0.94	0.638	0.631	0.127	0.217	0.145	0.085
			50	0.82	0.85	0.723	0.698	0.069	0.093	0.235	0.181
			100	0.74	0.78	0.801	0.760	0.050	0.080	0.293	0.193
			200	0.67	0.72	0.885	0.824	0.036	0.069	0.359	0.205
			500	0.59	0.65	1.01	0.912	0.023	0.052	0.504	0.244
			1000	0.53	0.60	1.12	0.988	0.016	0.046	0.644	0.258
			2000	0.47	0.54	1.26	1.09	0.011	0.032	0.831	0.327
109320	17% Carbon + 10% PVC	WB 0.5 min	3	1.10	----	0.539	-----	1.40	-----	0.015	-----
			10	0.91	0.92	0.652	0.645	0.532	0.590	0.034	0.031
			20	0.83	0.84	0.714	0.706	0.331	0.433	0.049	0.038
			50	0.73	0.76	0.812	0.780	0.184	0.315	0.079	0.048
			100	0.67	0.71	0.885	0.835	0.130	0.258	0.102	0.054
			200	0.62	0.67	0.956	0.885	0.088	0.203	0.139	0.065
			500	0.52	0.58	1.14	1.02	0.045	0.152	0.227	0.076
			1000	0.49	0.57	1.21	1.04	0.036	0.137	0.263	0.082
			2000	0.45	0.52	1.32	1.14	0.024	0.123	0.358	0.084

a Value under indicated pressure

b Value after release of indicated pressure - 3 psi remains

c Resistance of the sample (ohms) = 10X potential (volts) since 0.100 amp current used

h Voltage at 10 mA

Appendix Table A-4

CONSTANT CURRENT TESTS

Ref. No.	Cathode Materials (g/20 cm^2) DCA-70	SAB	CF	Blend	Separator Thickness (mils)	Electrolyte 2M $LiClO_4$ (ml/20cm^2)	Pressure (psi) Forming	Testing	Current Capacity (amp-min)	Current Density (mA/cm^2)	Average Volt(v)	Cathode Efficiency (%)	Energy Density (w-hr/lb)	Discharge Time(min)
105098	1.50	0.28	0.02	WB 0.5min	10	1.7	300	8	47.25	10	2.92	47.6	118.4	112.5
105099	1.50	0.28	0.02	WB 0.5	3	1.4	300	8	47.25	10	2.71	39.4	101.4	93
105100	0.375	0.07	0.005	WB 0.5	3	0.5	300	8	11.81	10	3.23	33.0	69.3	19.5
109304	1.50	0.28	0.02	WB 0.5	3	1.5	300	8	47.25	25	2.78	10.9	28.0	10.3
109305	1.50	0.28	0.02	WB 0.5	3	1.5	300	8	47.25	5	3.28	57.1	172.9	270
109306	1.50	0.28	0.02	WB 0.5	3	1.5	300	8	47.25	1	3.365	60.3	187.3	1425
109307	3.00	0.56	0.04	WB 0.5	3	2.7	300	8	94.50	10	3.29	13.9	46.2	65.5
109308	3.00	0.56	0.04	WB 0.5	3	2.7	300	8	94.50	10	3.00	15.9	48.3	75.0
109309	1.50	0.28	0.02	PK 1 hr	3	1.5	300	8	47.25	10	3.06	51.2	144.6	121
109310	1.50	0.28	0.02	BM 1 hr	3	1.5	300	8	47.25	10	3.01	38.5	107.0	96
109311	1.50	0.28	0.02	PK 8 hr	3	1.5	300	8	47.25	10	3.02	47.7	135.7	121
109312	1.50	0.28	0.02	PK 10 min	3	1.5	300	8	47.25	10	2.99	54.8	151.0	136
109313	1.50	0.28	0.02	WB 2 min	3	1.5	300	8	47.25	10	2.76	49.6	126.3	123.5
109314	1.50	0.28	0.02	WB 0.5min	3	1.5	300	8	47.25	10	2.77	52.1	133.2	130
109315	1.50	0.30	----	WB 0.5	3	1.5	300	8	47.25	10	3.15	57.0	165.8	142
109316	1.50	0.28	0.02	WB 0.5	3	1.5	300	8	47.25	10	3.15	58.1	168.7	144.5
109317	1.50	0.30	----	PK 10 min	3	1.5	300	8	47.25	10	3.18	57.9	169.7	144
109318	1.50	0.30[1]	----	PK 10 min	3	1.5	300	8	47.25	10	3.14	54.5	157.8	136
109320	1.50	0.30[2]	----	PK 10 min	3	1.7	300	8	47.25	10	3.19	59.9	166.4	149
109331	1.50	0.28	0.02	BM 10 min	3	1.5	300	8	47.25	10	3.07	55.0	155.9	130

[1] Uncompressed SAB used as received

[2] Screened 50% compressed (50 mesh screen)

Appendix Table A-5

CONSTANT CURRENT TESTS

Ref. No.	Cathode Materials (g/20 cm²) DCA-70	SAB	CF	Blend	Separator Thickness (mils)	Electrolyte 2M $LiClO_4$ (ml/20cm²)	Pressure (psi) Forming	Testing	Current Capacity (amp-min)	Current Density (mA/cm²)	Average Volt(v)	Cathode Efficiency (%)	Energy Density (w-hr/lb)	Discharge Time(min)
109323	1.50	0.28	0.02	PK 10min	3	1.5	300	8	47.25	37.5	2.59	12.9	30.8	8.1
109324	1.50	0.28	0.02	PK 10min	3	1.5[1]	300	8	47.25	37.5	2.59	9.4	21.7	5.9
109325	1.50	0.28	0.02	PK 10min	3	1.5[1]	300	8	47.25	25	2.89	15.9	40.7	15.0
109326	1.50	0.28	0.02	PK 10min	3	1.5[2]	300	8	47.25	10	2.94	29.5	82.8	69.8
109327	1.50	0.28	0.02	PK 10min	3	1.5[2]	300	8	47.25	25	2.13	4.1	8.4	3.9
109328	1.50	0.28	0.02	PK 10min	3	1.5[3]	300	8	47.25	25	2.70	24.6	62.3	23.3
109329	1.50	0.28	0.02	PK 10min	3	1.5[3]	300	8	47.25	10	2.88	40.5	109.0	95.6
109330	1.50	0.30[4]	----	PK 10min	3	1.8	300	8	47.25	10	3.17	56.3	151.2	133.0
109332	1.50[5]	0.28	0.02	WB 0.5min	3	1.5	300	8	47.25	10	3.17	55.4	161.9	130.8
109333	1.50	0.28	0.02	WB 0.5min	3	1.5	300	8	47.25	10	3.22	52.6	156.2	124.2
109334	1.50	0.28	0.02	WB 0.5min	3	1.5	300	8	47.25	10	3.20	52.9	156.2	125.0
109335	1.50	0.28	0.02	WB 0.5min	3	1.5	300	8	47.25	10	3.08	58.5	166.4	138.3
109336	1.50[6]	0.28	0.02	PK 10min	3	1.5	300	8	47.25	10	3.22	50.2	149.0	118.5
109337	1.50[7]	0.28	0.02	PK 10min	3	1.5	300	8	47.25	10	3.17	42.5	124.4	100.5
109338	1.50	0.28[8]	0.02	WB 5sec	3	1.5	300	8	47.25	10	3.18	56.7	166.3	133.9
109340	1.50	0.28	0.02	WB 5sec	3	1.7	300	8	47.25	10	3.05	56.1	149.1	132.6
109238[9]	1.315	0.246	0.018	PK 1hr	3	1.5	300	8	41.42	10	3.15	56.2	152.0	116.5
109239	1.50	0.28	0.02	WB 0.5min	3	1.5	300	8	47.25	10	3.23	54.0	160.8	127.5
109241[10]	1.203	0.224	0.016	PK 1hr	3	1.5	300	8	37.89	10	3.19	60.2	156.5	114.2
109242[11]	1.169	0.218	0.016	PK 1hr	3	1.5	300	8	36.82	10	3.14	57.7	145.2	106.3
109243[12]	1.17	0.22	0.016	PK 1hr	3	1.5	300	8	36.76	10	3.07	60.6	148.9	111.4
109246	1.50	0.28	0.02	WB 10sec	3	1.5	300	8	47.25	10	3.18	58.6	172.0	138.5
109247	1.50	0.28	0.02	WB 5sec	3	2.0	300	8	47.25	10	3.06	56.2	138.2	132.8
109248	1.50	0.30[13]	0.0	PK 10min	3	2.0	300	8	47.25	10	3.07	53.5	131.9	126.3
109250	1.50	0.30[13]	0.0	PK 10min	3	1.7	300	8	47.25	10	3.12	55.0	149.4	129.9
109251	1.50	0.28	0.02	PK 1hr	3	1.7	300	8	47.25	10	3.15	54.5	149.6	128.8
109253	1.50	0.28	0.02	PK 1hr	3	1.7	300	5.3	47.25	10	3.09	59.1	159.1	139.6
109257	1.50	0.28	0.02	PK 1hr	3	1.8	300	5.3	47.25	10	3.13	55.9	148.1	132.0

[1] 3M $LiClO_4$

[2] 1M $LiClO_4$

[3] 1.5M $LiClO_4$

[4] SAB screened through 50 mesh

[5] >400 mesh DCA-70

[6] +100 to -325 mesh

[7] <50 mesh

[8] SAB + CF WB for 10 sec

[9] Cathode pre-pressed and cut

[10] Cathode stored 1 week, ambient

[11] Li in Saran, 1 week ambient; new cathode

[12] Li and cathode in Aclar, 1 week ambient

[13] SAB screened through 20 mesh

Appendix Table A-6

CONSTANT VOLTAGE TESTS

Cell No.	System Component (g) DCA-70	SAB	CF	Electrolyte Type	ml	Pressure (psi) Form	Test	Blend min	Type	Theoretical Capacity (Amp-min)	Operating Voltage (Volts)	Discharge Time min.	Cathode Eff (%)	Energy Density (w-hr/lb)
109342	1.50	0.28	0.02	2M $LiAsF_6$	1.5	300	8	0.5	WB	47.25	3.2	30	15	43
												60	24.5	70
												120	34.0	97
												240	46.1	133
												480	60.9	175
												572	63.4	182
109343	1.50	0.28	0.02	2M $LiClO_4$	1.5	300	8	0.5	WB	47.25	3.2	30	23.6	69
												60	33.5	98
												120	45.5	134
												240	56.1	166
												480	64.0	189
												720	67.3	199
												1083	70.3	208
109345	1.50	0.28	0.02	2M $LiClO_4$	1.5	300	8	0.5	WB	47.25	3.0	30	23.6	68
												60	33.2	91
												120	43.6	121
												240	51.8	143
												480	59.2	164
												720	62.7	174
												1320	66.5	184
109346	1.50	0.28	0.02	2M $LiClO_4$	1.7	300	5.3	0.5	WB	47.25	3.2	30	23.5	65
												60	33.6	93
												120	47.2	132
												240	58.7	164
												480	64.8	181
												720	66.4	185
												1080	67.4	188
109347	1.50	0.47	0.03	2M $LiClO_4$	2.5	300	8	0.5	WB	47.25	3.2	30	20.3	44
												60	32.1	70
												120	46.6	102
												240	55.6	122
												480	48.9	129
												720	60.0	131
												1260	60.9	133
109348	1.50	0.47	0.03	2M $LiClO_4$	2.3	300	8	0.5	WB	47.25	3.2	30	25.8	59
												60	38.7	88
												120	55.3	127
												240	64.8	148
												480	68.0	156
												720	69.0	158
												1020	69.4	159
109349	1.50	0.28	0.02	2M $LiClO_4$	1.5	300	5.3	0.5	WB	47.25	3.2	30	23.4	69
												60	33.2	97
												120	46.0	136
												240	56.5	167
												480	62.5	185
												720	65.2	192
												1140	67.4	199

Table A-6 (Continued)

CONSTANT VOLTAGE TESTS

Cell No.	System Component (g) DCA-70	SAB	CF	Electrolyte Type	ml	Pressure (psi) Form	Test	Blend min	Type	Theoretical Capacity (Amp-min)	Operating Voltage (Volts)	Discharge Time min.	Cathode Eff (%)	Energy Density (w-hr/lb)
109350	1.50	0.28	0.02	2M $LiClO_4$	1.4	300	5.3	0.5	WB	47.25	3.2	30	21.2	64
												60	29.3	89
												120	38.9	118
												240	46.3	141
												480	52.3	159
												720	55.8	170
												1200	59.5	181
109351	1.50	0.28	0.02	2M $LiClO_4$	1.4	300	8	0.5	WB	47.25	3.2	30	23.1	70
												60	32.8	99
												120	46.0	140
												240	58.1	177
												480	64.5	196
												720	67.3	205
												1080	69.1	210
												1320	69.8	212
109353	1.50	0.28	0.02	2M $LiClO_4$	1.5	300	8	10	PK	47.25	3.2	30	18.5	54
												60	31.6	93
												120	46.7	138
												240	60.3	178
												480	67.6	200
												720	69.7	206
												1020	70.7	209
109354	1.50	0.28	0.02	2M $LiClO_4$	1.5	300	8	0.16	WB	47.25	3.2	30	23.1	68
								also carbons				60	34.7	102
								0.16	WB			120	50.5	149
												240	62.3	184
												480	68.7	203
												720	70.8	209
												1080	72.3	213
109355	1.50	0.28	0.02	2M $LiClO_4$	1.5	300	8	60	PK	47.25	3.2	30	22.0	65
								also carbons				60	34.2	101
								0.16	WB			120	49.4	146
												240	61.8	183
												480	67.4	199
												720	69.2	204
												1080	70.3	208
109356	1.50	0.28	0.02	2M $LiClO_4$ chilled to 4°C prior to using. Temp rose to 15.5°C by the time cell was completely assembled	1.4	300	8	0.16	WB	47.25	3.2	30	22.4	68
								also carbons				60	32.2	98
								0.16	WB			120	44.2	135
												240	56.4	171
												480	64.6	197
												720	67.5	205
												1080	69.2	211
109357	1.50	0.28	0.02	3M $LiAsF_6$	1.5	300	8	0.5	WB	47.25	3.2	30	21.7	61
												60	31.0	88
												120	38.4	110
												240	50.1	143
												480	60.4	172
												720	63.6	182
												1080	65.4	187
109358	1.50	0.28	0.02	3M $LiAsF_6$	1.45	300	8	0.5	WB	47.25	3.2	30	20.4	59
												60	28.0	81
												120	35.9	104
												240	44.0	128
												480	58.2	169
												720	64.3	187
												1080	68.8	200

Appendix Table A-7

CONSTANT CURRENT TESTS

Ref. No.	Cathode Materials (g/20 cm²) DCA-70	SAB	CF	Blend	Separator Thickness (mils)	Electrolyte 2M $LiClO_4$ (ml/20cm²)	Pressure (psi) Forming	Testing	Current Capacity (amp-min)	Current Density (mA/cm²)	Average Volt(V)	Cathode Efficiency (%)	Energy Density (w-hr/lb)	Discharge Time(min)
109257	1.5	0.28	0.02	PK/1hr	3	1.8	300	5.3	47.25	10	3.13	55	148	132
109258[a]	1.5	0.28	0.02	PK/10min	3	1.5	300	8	47.25	10	2.78	42	106	101
109259	1.5	0.28	0.02	PK/1hr	3	1.8	100	5.3	47.25	10	3.09	59	156	141
109262[1]	1.5	0.28	0.02	PK/1hr	3	1.7	300	8	47.25	10	3.12	59	162	141
109263	1.5	0.307	0.022	PK/1hr	3	2.5	300	5.3	47.25	10	3.10	62	133	148
109268[2]	1.34	0.251	0.018	PK/1hr	3	1.5	300	8	42.37	10	3.12	56	152	119
109271[3]	1.31	0.246	0.018	PK/1hr	3	1.5	300	8	41.45	10	3.10	59	158	123
109272[3]	1.32	0.248	0.018	PK/1hr	3	1.5	300	8	41.83	10	3.03	54	142	114
109273[4]	1.32	0.247	0.018	PK/1hr	3	1.5	300	8	41.58	10	2.99	56	144	117
109274[4]	1.35	0.252	0.018	PK/1hr	3	1.5	300	8	42.53	10	3.23	54	154	116
109275[5]	1.32	0.247	0.018	PK/1hr	3	1.5	300	8	41.58	10	3.09	59	158	124
109276[6]	1.43	0.267	0.019	PK/1hr	3	1.5	300	8	45.05	10	2.91	49	130	112
109277[7]	1.34	0.250	0.018	PK/1hr	3	1.5	300	8	42.26	10	3.09	58	156	123
109278[8]	1.31	0.245	0.018	PK/1hr	3	1.5	300	8	41.25	10	3.14	42	115	87
109279[8]	1.32	0.247	0.018	PK/1hr	3	1.5	300	8	41.58	10	3.13	48	131	101
109280[2]	1.32	0.247	0.018	PK/1hr	3	1.5	300	8	41.58	10	3.06	57	150	119
109282	1.5	0.307	0.022	PK/1hr	3	2.5	300	5.3	47.25	25	2.58	27	49	26
109283[9]	1.26	0.235	0.017	PK/1hr	3	1.5	300	8	39.69	10	3.14	61	162	122
109284[9]	1.30	0.243	0.017	PK/1hr	3	1.5	300	8	40.95	10	3.09	55	147	114
109285[10]	1.32	0.246	0.018	PK/1hr	3	1.5	300	8	41.58	10	3.13	55	150	115
109289[11]	0.45	0.56	0.04	WB/1min	3	3.0	300	8	14.18	10	3.22	40	28	28
109290[12]	0.45	0.56	0.04	WB/1min	3	3.0	300	8	14.18	10	2.50	28	15	8
109291	1.5	0.28	0.02	PK/1hr	3	1.5	300	6	47.25	10	2.67	52	136	123
109292[11]	0.19	0.28	0.02	WB/1min	3	1.3	300	8	6.15	10	3.04	25	15	7
109294[11]	0.19	0.28	0.02	WB/1min	3	1.3	300	8	6.15	5	3.43	35	24	22
109295	1.50	0.28	0.02	PK/1hr	3	1.5	300	8	47.25	10	3.14	53	156	127
109296[11]	0.19	0.28	0.02	WB/1min	3	1.3	300	8	6.15	5	2.88	28	16	17
109297[12]	1.50	0.28	0.02	WB/0.5min	3	1.7	300	8	47.25	10	3.25	49	135	117
109298[13]	1.24	0.234	0.017	PK/1hr	3	1.5	300	8	39.06	10	3.12	57	149	112
109299[13]	1.23	0.224	0.017	PK/1hr	3	1.5	300	8	38.75	10	2.96	60	146	116
109300[14]	1.48	0.274	0.019	PK/1hr	3	1.5	300	8	46.62	10	2.66	29	71	68

[a] 3M $LiClO_4$

[1] 0.35g Graphite at base

[2] Li-Aclar/1wk (ST + H)*/new cathode

[3] Cell-Aclar/1wk ST + H

[4] Li-wax/1wk ambient

[5] Li-Aclar/1wk/cathode/1wk ambient

[6] Li-Aclar/1wk/cathode/1wk ST + H

[7] Cell-Aclar/1wk ambient

[8] Li-wax/1wk ST + H

[9] Cell-Aclar/4wk Ambient

[10] Li-Aclar/4wk ambient/new cathode

[11] DCA-70 in electrolyte, 15 wt %

[12] Blended 0.15g $LiPF_6$ in mix

[13] Cell-Aclar/4wk ST + H

[14] Li-Aclar/4wk ST + H/new cathode

• 70°F/50% relative humidity

Appendix Table A-8

CONSTANT CURRENT TESTS

Ref. No.	Cathode Materials (g/20 cm^2) DCA-70	SAB	CF	Blend	Separator Thickness (mils)	Electrolyte 2M $LiClO_4$ (ml/20cm^2)	Pressure (psi) Forming	Testing	Current Capacity (amp-min)	Current Density (mA/cm^2)	Average Volt(V)	Cathode Efficiency (%)	Energy Density (w-hr/lb)	Discharge Time(min)
110701[1]	1.5	0.28	0.02	PK/1hr	3	1.5	300	8	47.25	10	2.79	32	82	76
110702[2]	1.33	0.248	0.017	PK/1hr	3	1.5	300	8	41.89	10	3.14	58	158	122
110703[3]	1.35	0.253	0.017	PK/1hr	3	1.5	300	8	42.53	10	3.07	51	136	108
110704[3]	1.38	0.261	0.018	PK/1hr	3	1.5	300	8	43.47	10	2.3	2	3	3.5
110705[4]	1.35	0.253	0.017	PK/1hr	3	1.5	300	8	42.53	10	2.97	51	131	108
110706-1[5]	1.34	0.250	0.017	PK/1hr	3	1.5	300	8	42.10	10	2.87	7	8	15
110706-2[5]	1.35	0.253	0.017	PK/1hr	3	1.5	300	8	42.53	10	----	0	0	0
110717[6]	1.50	0.28	0.02	WB/30sec	3	(1.8)[6]	300	8	47.25	10	3.25	50	132	117
110718[6]	1.50	0.28	0.02	WB/30sec	3	1.6[6]	300	8	47.25	25	2.99	8	25	9
110720[6]	1.50	0.28	0.02	WB/30sec	3	1.5[6]	300	8	47.25	10	3.21	51	146	120
110722[7]	1.50	0.28	0.02	WB/30sec	3	1.5[7]	300	8	47.25	10	3.28	52	153	123
110723[7]	1.50	0.28	0.02	WB/30sec	3	(1.8)[7]	300	8	47.25	25	3.33	11	32	11

[1] Li Ambient/6hrs - new cathode

[2] Li (Aclar) and cathode ambient/1 mo

[3] Li (Wax)/1 mo ambient

[4] Li (Aclar)/1 mo 70°F/50% Rel. Hum.

[5] Li (Wax)/1 mo 70°F/50% Rel. Hum.

[6] 2M $LiAsF_6$

[7] 3M $LiAsF_6$

Appendix Table A-9

CONSTANT CURRENT TESTS

Ref. No.	Cathode Materials (g/20 cm^2) DCA-70	SAB	CF	Blend	Separator Thickness (mils)	Electrolyte 2M $LiClO_4$ (ml/20cm^2)	Pressure (psi) Forming	Testing	Current Capacity (amp-min)	Current Density (mA/cm^2)	Average Volt(V)	Cathode Efficiency (%)	Energy Density (w-hr/lb)	Discharge Time(min)
110735[1]	1.34	0.250	0.017	PK/1 hr	3	1.5	300	8	42.21	10	3.14	56.0	152	117.8
110736[1]	1.36	0.250	0.017	PK/1 hr	3	1.5	300	8	42.84	10	3.09	57.0	155	123.0
110737[2]	1.10	0.200	0.015	PK/1 hr	3	1.5	300	8	34.49	10	3.17	53.2	129	91.2
110738[3]	1.35	0.233	0.017	Pk/1 hr	3	1.5	300	8	42.56	10	3.13	54.7	149	116.5
110745[4]	1.23	0.230	0.016	PK/1 hr	3	1.5	300	8	38.84	10	3.11	59.3	153	115.2
110746[4]	1.23	0.229	0.016	PK/1 hr	3	1.5	300	8	38.84	10	3.14	58.7	153	114.0
110747[5]*	1.40	0.262	0.019	PK/1 hr	3	1.5	300	8	44.23	10	2.88	48.8	125	108.0
110751[6]**	1.42	0.266	0.019	PK/1 hr	3	2.0	300	8	44.73	10	2.86	23.0	51	51.5

[1][Cath + Li] Aclar/3 mo-ambient

[2]Li(Aclar) + Cath/3 mo-ambient

[3]3 mo Li(Aclar) + new Cath-ambient

[4][Cath + Li] Aclar/3 mo - 70°F/50% rel. hum.

[5]3 mo-Li (Aclar) + new Cath - 70°F/50% rel. hum.

[6]3 mo-Li (Aclar) + Cath/3 mo - 70°F/50% rel. hum.

* Inadvertently left on open circuit 1 hr before load was applied.

** No operation on 1.5 ml. Hence, addition of 0.5 ml more. Cathode activity is 69% of new cathode.